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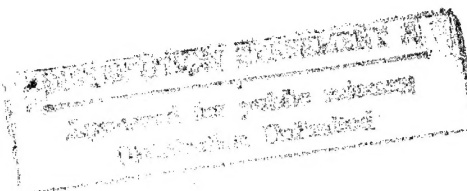# NR-150B2 Adhesive Development

P. S. Blatz

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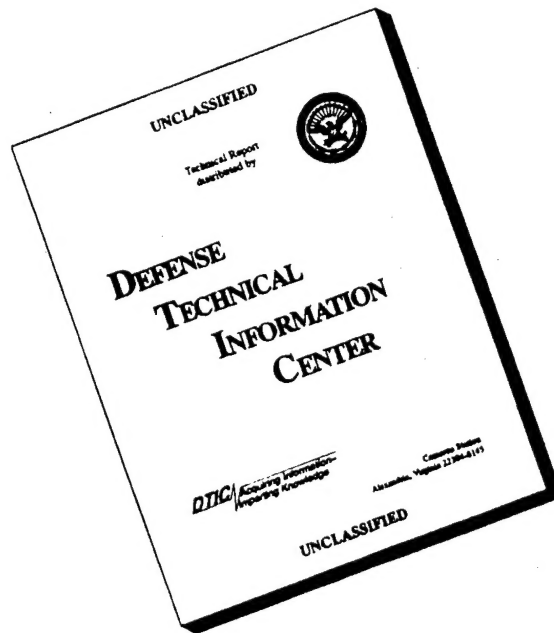
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NR-150B2 Adhesive Development

P. S. Blatz
E. I. du Pont de Nemours & Co., Inc.
Wilmington, Delaware

NASA

National Aeronautics
and Space Administration

**Scientific and Technical
Information Office**

1978

FOREWORD

The Research and Development Division of the Plastic Products and Resins Department of the Du Pont Company was responsible for the work performed in this study. Dr. P. S. Blatz, Research Associate, was responsible for carrying out all phases of the work. Dr. Warren J. Brehm was the program manager, and Dr. Hugh H. Gibbs was used as a consultant. The contract administrators were Mr. Wayne McCabe during the early part of the program and Mr. Carl H. Jepson for the latter part.

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ABBREVIATIONS

6FTA 2,2 bis(3',4'-dicarboxyphenyl) hexafluoropropane

PPD para-phenylenediamine

MPD meta-phenylenediamine

ODA oxydianiline

NMP N-methylpyrrolidone

Diglyme dimethyl ether of diethylene glycol

Tg glass transition temperature

O.T. onset temperature (Section 3.2)

TMA thermomechanical analysis

SUMMARY

This document is the final program report describing work performed by the Plastic Products and Resins Department of E. I. du Pont de Nemours and Company, Inc. for the National Aeronautics and Space Administration, Langley Research Center under Contract NAS1-14620. The objective of this program was to conduct research and development aimed at developing NR-150B2 polyimide resin into an adhesive for bonding high temperature graphite/polymer matrix composites. The adhesive was to be designed to have the durability for 125-500 hours at 589 K (600°F) in air and to have a significant improvement in processibility not previously obtained with high temperature aromatic condensation polyimide adhesives.

The objective was accomplished by: (1) evaluating variations in the monomer solution stoichiometry as it affects the flow and glass transition temperature (Tg) of the polyimide resin derived from the solution, (2) optimizing the bonding conditions within the limits obtainable in commercial production autoclaves, (3) demonstrating the capability of the newly defined adhesive composition and process using titanium adherends. The utility of the adhesive was then demonstrated by: (a) exposing lap shear samples prepared using graphite fiber/NR-150B2 adherends to four different environments; (b) preparing and evaluating wide area bonds and face sheet/honeycomb core flatwise tensile specimens; and (c) evaluating adhesive crack propagation at 589 K (600°F).

During task 1, it was found that improved resin flow at significantly lower adhesive prepreg volatile levels leading to low void level adhesive bond lines could only be obtained using an adhesive resin with a Tg well below 589 K (600°F) and, therefore, unsuitable for use at that temperature.

In task 2, it was found that no combination of autoclave bonding and free-standing post cure conditions could be found which produced acceptable lap shear bonds at both R.T. and 589 K

using NR-150 polyimide adhesive systems based on N-methylpyrrolidone (NMP) as the solvent. However, replacement of the NMP with diglyme (the dimethyl ether of diethylene glycol) in the adhesive system resulted in a dramatic improvement in processibility of the adhesive and the attainment of acceptable bond strengths at both R.T. and 589 K (600°F).

The utility of the newly developed NR-150 adhesive system was demonstrated in task 3. Lap shear samples, prepared from composite adherends, were exposed to the following environments: 500 hours in 589 K (600°F) air; 35 days in 322 K (120°F) 95% RH; 34 days immersed in JP-4 jet fuel at R.T.; and 34 days immersed in methyl ethyl ketone (MEK) at R.T. These studies indicated that this new adhesive bond had excellent resistance to these environments.

Evaluation of bonding wide areas using this adhesive indicated that acceptable bond strengths could only be obtained using abnormally long cure cycles in order to allow diffusion of the volatiles out of the bond line.

Flatwise tensile specimens prepared using composite face sheets and titanium honeycomb core had low strengths because of poor techniques in curing the primer coating on the honeycomb cell edge. More effort will be required to produce honeycomb sandwich panels with the flatwise tensile strength levels expected from this new adhesive.

A wedge-type crack propagation test at 589 K (600°F) using 3.175 mm (1/8") thick unidirectional graphite fiber/NR-150B2 adherends confirmed the excellent toughness and stability of the new NR-150 adhesive.

The results of these tests indicate that the newly developed experimental adhesive has potential as a high temperature adhesive for use in the harsh environments to which jet engine parts, high performance military aircraft, and space vehicles are exposed.

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1. INTRODUCTION

This final report presents work accomplished by E. I. du Pont de Nemours and Company, Inc. for the National Aeronautics and Space Administration, Langley Research Center under Contract NAS1-14620 during the period September 16, 1976, through November 16, 1977. The objective of this program was to develop a polyimide resin derived from NR-150B2 precursor solution into an adhesive for bonding high temperature graphite fiber/polymer matrix composites.

Several adhesives have been available for some time on either a commercial or experimental basis for use at high temperatures.[1-10] Most of these adhesives, however, suffer from one or more of the following deficiencies:

(a) The adhesive requires long and involved processing cycles.

(b) The adhesive contains volatiles which produce adhesive bond lines with undesirable voids.

(c) The adhesives are thermosetting and are, therefore, characterized by brittleness and poor crack resistance.

(d) The adhesive does not have good strength at 589 K (600°F).

(e) The adhesive has good initial 589 K (600°F) strength, but the bond strengths degrade severely after exposure to 589 K for some time.

(f) The adhesives do not consistently give good bond strengths.

With the introduction of NR-150 polyimide precursor solutions,[11] a polyimide system has become available which has the potential to eliminate many of the problems of the high temperature adhesives indicated above. Upon heating NR-150 solutions an aromatic polyimide is formed which is a linear non-crosslinked polymer having a high degree of thermoplasticity. The aromatic character of the polymers result in excellent stability at least to 589 K (600°F). The thermoplasticity has

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the potential to give flow during processing resulting in reduced void levels and to give toughness resulting in excellent resistance to crack propagation.

As structural adhesives for both primary and secondary bonding are needed for the Space Shuttle, it was apparent that an adhesive based on NR-150B2 polyimide precursor solutions might very well be a good candidate for these applications.[12] The high temperatures and the high degree of reliability required indicated that an adhesive with the characteristics of NR-150 systems should be developed and evaluated.

Use of commercial products or names of manufacturers in this report does not constitute endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

2. REQUIRED BONDING PROCEDURES

For an adhesive to be useful for all types of applications, it must be applicable for bonding small as well as larger structures. NASA required that the adhesive to be developed under this program should be useful for bonding in large production autoclaves. The processing conditions used in this program were chosen to be applicable to a large autoclave.

Although most of the adhesive bonding evaluations in this program were made using a small laboratory press, processing conditions were chosen to simulate that used in an autoclave. The following conditions were utilized with a vacuum bag assembly as follows:

(a) A maximum heating rate of .047 K/second (5°F/min.).

(b) A maximum pressure of 1.38 MPa (200 psi).

(c) A maximum bonding temperature of 589 K (600°F).

For most of the work, full vacuum (757 mm) was used during the bonding cycle, and except where indicated, a total bonding cycle of at most 288 Ks (8 hours) duration was used. Free standing post cures in air up to a maximum temperature of about 644 K (700°F) were used.

3. UNFILLED ADHESIVE RESIN EVALUATION

The objective of the first task was to determine if, by chemically modifying the commercially available NR-150B2G adhesive solution, an adhesive prepreg film could be developed which: (1) has improved flow at significantly lower volatile levels and, therefore gives acceptable room temperature (R.T.) lap shear strengths, and (2) has an adhesive resin glass transition temperature (Tg) above 589 K (600°F), thereby also giving acceptable 589 K lap shear strengths.

The commercially available NR-150B2G polyimide precursor adhesive solution was used as the control composition. This solution consists of a 1:.95:.05 mole ratio of 6FTA* to PPD* to MPD*, at a concentration of 48 wt. % cured resin solids in NMP*.

To obtain improved flow, the 6FTA:diamine ratio was changed to a maximum of 6% excess tetraacid and the ratio of PPD/MPD diamines was changed to a minimum of 50:50.

3.1 EXPERIMENTAL PROCEDURES

Because of the expense and unavailability of graphite fiber/polyimide composite panels, the initial adhesive composition scouting work was carried out using 6 AL-4 V titanium alloy 1.27 mm (50 mils) thick standard lap shear coupons. The titanium surface was etched using "Pasajell" 107 for improved adhesion using the procedure in Appendix A and was primed with the adhesive solution using the procedure in Appendix B, Part I.

The adhesive prepreg was prepared by soaking 112 Style E glass scrim cloth in the neat resin solution (containing 48 wt. % cured resin solids) warmed to 334-343 K (140-158°F) then passing the coated fabric immediately through opposed Gardner coating knives set at .38-.76 mm (15-30 mil) air gap to obtain prepreg of the desired thickness. The prepreg was then "B" staged in an air circulated oven for 3.6 Ks (1 hour) at 418 K (293°F) and successively at 433 K (320°F) and 453 K (356°F) for periods of time necessary to obtain the desired prepreg volatiles content.

*See list of abbreviations at beginning of report.

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Lap shear samples of the simple overlap type were prepared using a laboratory press having .203 m x .203 m (8" x 8") platens capable of being heated to at least 700 K (800°F). Four samples were bonded simultaneously using a 4-finger coupon (cut from the commercially available 5-finger coupon) with a suitable holder on a vacuum plate with breather plys of glass fabric, high temperature tape sealant, and .05 mm (2 mil) Kapton® film as the vacuum bag. The vacuum was supplied by a laboratory mechanical vacuum pump protected with a dry ice trap which produced a vacuum of at least .757 m (29.8") of mercury. Two primed titanium coupons were sandwiched on either side of adhesive prepreg to produce four 25.4 mm (1 inch) wide by 127 mm (1/2") long bonds.

The bonding cycle used for this exploratory work is as follows:

(a) Heat the lap shear assembly from R.T. to 589 K (600°F) at .033 K/second (2 K/minute) under full vacuum and 1.38 MPa (200 psi).

(b) Bond for 1.8 Ks (30 min.) at 589 K (600°F) under full vacuum, 1.38 MPa (200 psi).

(c) Hold for 3.6 Ks (1 hour) at 589 K under full vacuum, zero pressure.

(d) Cool at about .22 K/second (23.4°F/minute) to 323 K (50°C) under full vacuum, zero pressure.

The Tg of the completely cured resin in the adhesive prepreg is measured using a Du Pont 990 analyzer with a thermo-mechanical analyzer attachment on a laminate prepared from the adhesive prepreg using the molding procedure in Appendix C.

3.2 EFFECT OF MONOMER IMBALANCE AND DIAMINE RATIO

NR-150 polyimide precursor solutions were prepared with a monomer imbalance of 1 1/2%, 3% and 6 mole % excess 6FTA and with a PPD/MPD mole ratio of 95/5, 75/25, 60/40, and 50/50. Solutions were also prepared using ODA* in place of MPD.

*See list of abbreviations at beginning of report.

The results of thermomechanical analysis (TMA) of well-cured moldings from the various adhesive solutions are given in Table I and Figure 1. Included in the Table is the Tg as well as the onset temperature (O.T.) of the resin. The O.T. is the temperature at which the TMA curve begins to deviate from a straight line as the temperature increases. The difference between the O.T. and Tg gives a qualitative measure of the resin cure. The smaller the difference, the better the resin cure. The TMA curve of a well-cured NR-150B2G/glass cloth laminate is shown in Figure 2.

From the data in Table I and Figure 1, it can be concluded that:

(1) With the specific molding procedure used, polymer from the commercial NR-150B2G adhesive solution has an onset temperature and Tg of 623 K (662°F) and 633 K (680°F), respectively. This is a typical result for this composition.

(2) Reducing the polymer molecular weight by adding an excess of the tetraacid or increasing the mole ratio of MPD results in a decrease in the polymer Tg.

(3) Reducing the molecular weight of the polyimide by the addition of a 6% excess of 6FTA (giving a calculated degree of polymerization of 33.4 and molecular weight of 17,234) reduces the Tg of the polymer by 30 K (54°F).

(4) Increasing the concentration of MPD from 5% to 25% based on total diamines reduces the Tg of the polymer by only 8 K (14°F).

(5) Since the effects of the addition of an excess of 6FTA and an increase in MPD concentration are additive, combining the two modifications causes a profound decrease in the Tg of the resulting polymer.

(6) Replacement of MPD by ODA as the co-diamine shows an effect similar to MPD on the Tg.

TABLE I.

EFFECT OF ADHESIVE SOLUTION CHEMICAL COMPOSITION ON
ONSET TEMPERATURE AND TG OF RESULTING POLYIMIDE

Solution Composition		Molded Prepreg	
Monomer Ratio	Diamine Ratio	Onset Temp.	Tg
1:1 6FTA:Diamine	95/5 PPD/MPD	623K(662°F)	633K(680°F)
6% Excess 6FTA	95/5 PPD/MPD	563K(554°F)	603K(626°F)
1:1 6FTA:Diamine	75/25 PPD/MPD	618K(653°F)	625K(666°F)
3% Excess 6FTA	75/25 PPD/MPD	593K(608°F)	603K(626°F)
1 1/2% Excess 6FTA	50/50 PPD/MPD	573K(572°F)	588K(598°F)
3% Excess 6FTA	50/50 PPD/MPD	573K(572°F)	578K(589°F)
6% Excess 6FTA	50/50 PPD/MPD	538K(509°F)	566K(560°F)
3% Excess 6FTA	75/25 PPD/ODA	589K(614°F)	603K(626°F)
3% Excess 6FTA	85/15 PPD/ODA	608K(635°F)	613K(644°F)

The objective was to select a solution composition which
produces adhesive prepreg giving acceptable lap shear strengths
at 589 K-horizontal dashed line in Figure 1. Compositions of
interest, therefore, are above that line.

FIGURE 1
EFFECT OF CHEMICAL COMPOSITION
OF NR-150 TYPE POLYIMIDES ON POLYMER Tg
(6 FTA/PPD/CO-DIAMINE SYSTEMS)
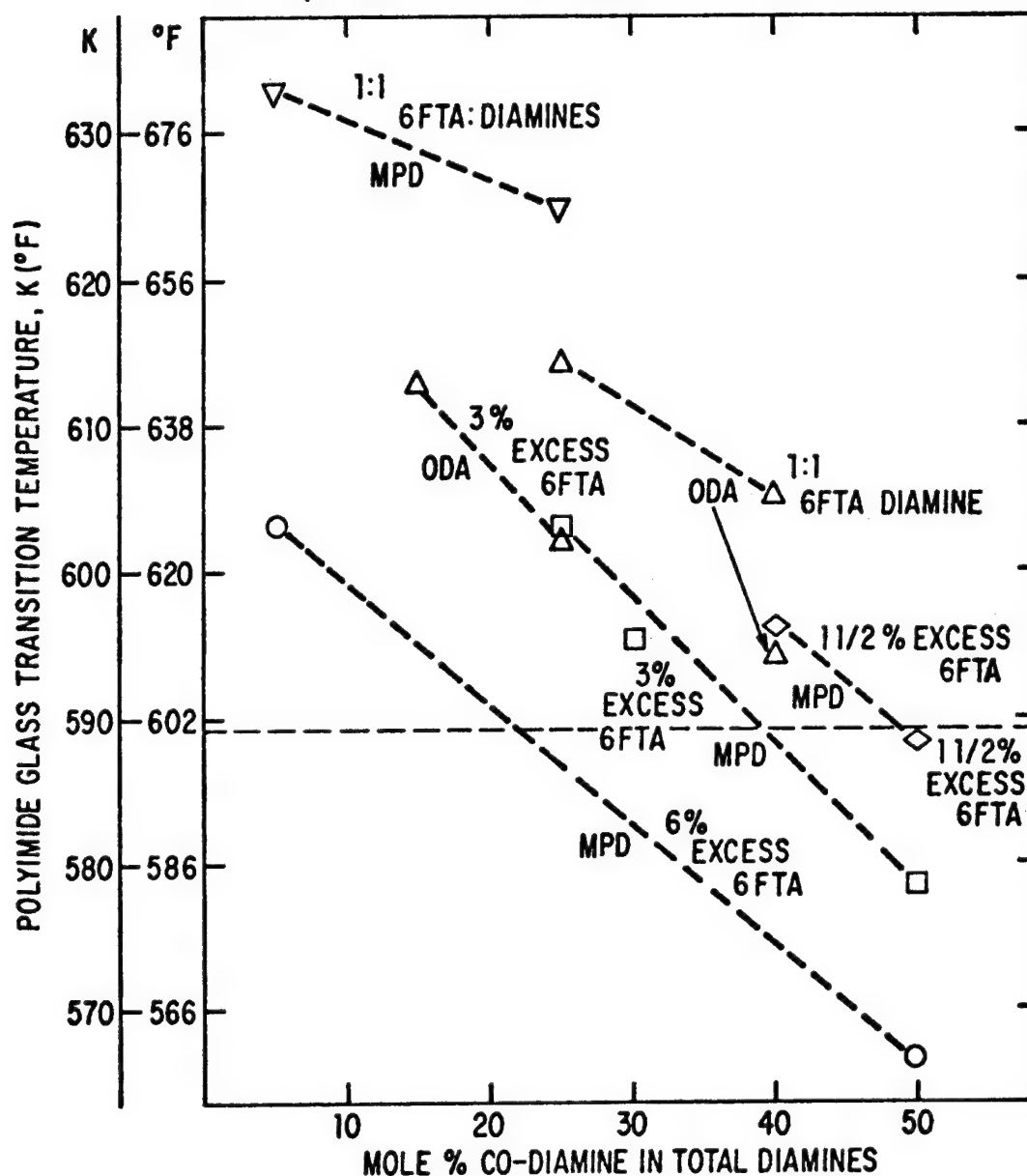
FIGURE 2
TMA CURVE OF
LAMINATE MOLDED FROM
NR-150B2G/GLASS CLOTH ADHESIVE PREPREG
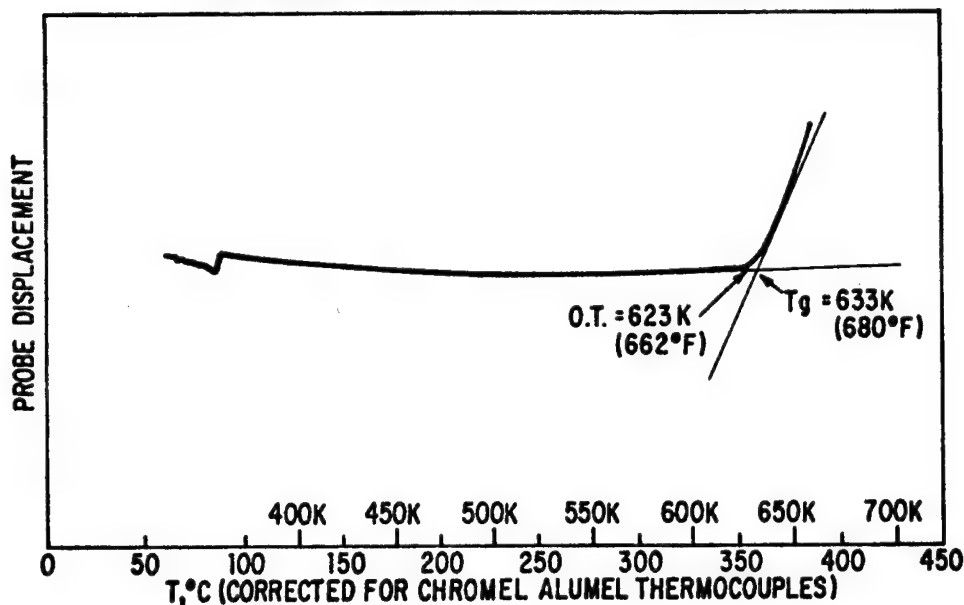
The changes in the chemical composition of the adhesive solution not only affect the Tg of well-cured resin derived from these solutions, but also the resin flow during bonding and the polymer toughness. A qualitative measure of the polymer toughness has been observed during the preparation of prepreg from these solutions. It was observed that compositions with 6% excess 6FTA produce prepreg having many resin cracks with some of the polymer flaking off on bending the prepreg. Solutions with 1 1/2% or 3% excess 6FTA produce prepreg with few or no cracks depending on volatile content. It appears that polymer from solutions containing 6% excess 6FTA, having a calculated molecular weight of 17,234, is brittle and would probably not produce tough, resilient bond lines.

Adhesive prepreg prepared from solutions containing 6 mole % excess of 6FTA and a 50/50 ratio of PPD/MPD exhibit significantly improved flow characteristics but as expected poor 589 K (600°F) lap shear strengths as indicated in Tables II and III.

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TABLE II.

COMPARISON OF PREPREG PROPERTIES AND LAP SHEAR STRENGTHS AT ROOM TEMPERATURE USING TWO DIFFERENT ADHESIVE SOLUTIONS

Adhesive Solution Used (No Filler)	Volatiles Content of Prepreg	Resin at Bond Line of Tested Lap Shear Sample		Ti/Ti Bonds Lap Shear Strength at R.T.	Resin Squeeze-Out at Bond Line
		Onset Temp.	Tg		
				(avg. of 4 samples)	
NR-150B2G adhesive solution 1:1 mole ratio 6FTA:Diamine 95/5 PPD/MPD	13.9%	603 K (626°F)	609 K (636°F)	16.95 MPa (2458 psi)	slight
"	14.4%	603 K (626°F)	619 K (655°F)	14.23 MPa (2064 psi)	moderate
adhesive solution containing 6% excess 6FTA 50/50 PPD/MPD	6.3%	(not determined)		13.91 MPa (2018 psi)	slight
"	7.2%	414 K (286°F)	427 K (310°F)	16.13 MPa (2340 psi)	moderate

TABLE III.

LAP SHEAR STRENGTHS AT 316°C (600°F)

Adhesive Solution Composition	Prepreg Volatiles Content	Titanium/Titanium Lap Shear Strength at 589 K (600°F) Average of 4 Samples
NR-150B2G adhesive solution, 1:1 6FTA: Diamine 95/5 PPD/MPD	14.4%	4.60 MPa (667 psi)
"	14.8%	4.97 MPa (721 psi)
"	15.2%	5.20 MPa (754 psi)
Adhesive solution containing 6% excess 6FTA, 50/50 PPD/MPD	8.1%	0.72 MPa (104 psi)

Comparison of the adhesive prepreg volatiles content, the adhesive resin Tg at the bond line, the lap shear strength obtained on bonding titanium adherends, and the resin squeeze-out at the bond line is made in Table II for the commercially available NR-150B2 composition (monomer mole ratios of 1:.95:.05 6FTA:PPD:MPD) and the experimental 6 mole % excess 6FTA; 50/50 PPD/MPD mole ratio. A prepreg volatile content of only about 6-8% is required to produce adequate flow using the experimental composition as compared to about 14% for the commercially available composition with equivalent flow and lap shear strength. However, as indicated in Table III, the 589 K (600°F) lap shear strength of a bond prepared using the experimental adhesive composition is very poor and well below that obtained using the control composition.

3.3   INITIAL PREFERRED ADHESIVE COMPOSITION ADHESIVE CONTAINING MPD

From the information presented above, it is apparent that the preferred adhesive composition should have a cured resin Tg above 589 K and a monomer imbalance no greater than 3 mole % excess 6FTA.

Three compositions indicated in Table IV were chosen as the most likely candidates for meeting the requirements of an optimum NR-150 adhesive composition.

Solution composition A, Table 4, was chosen for evaluation first. Prepreg was prepared from the solution according to the procedure described in Section 3.1. Lap shear bonds were prepared with titanium adherends using the procedure also described in Section 3.1 with the results of tests on the samples indicated in Table 5. The bonding procedures for the four samples in the Table were identical except for the post cure conditions which were carried out immediately after the 1.8 Ks (30 minutes) bonding at 1.38 MPa (200 psi). This post cure step varied in time from 3.6 Ks (1 hour) to 7.2 Ks (2 hours) and in temperature from 589 K (600°F) to 644 K (700°F). A free standing air post cure was

not used in this study. The post cure conditions, bond line thickness, adhesive bond line resin Tg and O.T. and the average R.T. lap shear strength are given in Table V.

TABLE IV

GLASS TRANSITION TEMPERATURE (Tg) AND
ONSET TEMPERATURE (O.T.) OF MOLDINGS
FROM ADHESIVE PREPREG BASED ON
CANDIDATE SOLUTIONS

	Solution Composition	Onset Temperature of Molding	Tg of Molding
A.	1 1/2% excess 6FTA* 60/40 PPD/MPD 48 wt. % in NMP	595K(612°F)	596K(614°F)
B.	3% excess 6FTA 70/30 PPD/MPD 48 wt. % in NMP	583K(509°F)	593K(608°F)
C.	1 1/2% excess 6FTA 60/40 PPD/ODA 48 wt. % in NMP	588K(598°F)	594K(610°F)

*See list of abbreviations at beginning of report.

The results indicate that:

(1) A prepreg volatile content of about 9 1/2% is required to produce acceptable adhesive flow during the bonding operation. This is above the hoped for 6-8% level required for the initially evaluated lower molecular weight composition in Tables II and III.

(2) R.T. lap shear strengths of 20.68 MPa (3000 psi) to 27.58 MPa (4000 psi) are readily obtained on post curing under full vacuum for up to 7.2 Ks (2 hours) at 589 K (600°F) (see Samples 9, 10, 11, Table V).

(3) These high lap shear strengths are obtained with bond line thicknesses of .127 mm to .254 mm (5-10 mils) a thickness range which has been found by others[2] to give optimum bond strengths.

(4) Although post curing in a vacuum bag at 589 K produces high R.T. lap shear strengths, the Tg of the resin in the bond line is well below the 589 K necessary to give acceptable 589 K

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TABLE V.

LAP SHEAR STRENGTHS AT ROOM TEMPERATURE OF POLYIMIDE BONDED 6/4 TITANIUM

Adhesive solution composition: 1 1/2% excess 6FTA, 60/40 PPD/MPD
Bonding Conditions: 1.8 Ks (30 minutes) 589 K (600°F), full vacuum, 1.38 MPa (200 psi)

Prepreg volatile content: ~9.5%

Lap Shear Sample #	Post Cure Conditions (full vacuum only)	Bond Line Thickness mm (mils)	Resin at Bond Line K(°F) O.T.	Resin at Bond Line K(°F) Tg	Lap Shear Strength R.T. Average of 4 (high and low) MPa	psi
9	3.6 Ks (1 hr.) 589 K	.178-.254 (7.0-10.0)	533 (500)	553 (536)	24.6 (21.8-27.1)	3568 (3160-3923)
10	"	.140-.203 (5.5- 8.0)	498 (437)	508 (455)	24.1 (22.7-25.2)	3490 (3298-3602)
11	7.2 Ks (2 hrs.) 589 K (600°F)	.139-.165 (5.5- 6.5)	533 (500)	563 (554)	26.2 (23.6-28.4)	3802 (3426-4117)
12	.9 Ks (15 mins.) 589 K→644 K (600°F)(700°F) then 6.3 Ks (1 1/4 hrs.) 644 K (700°F)	.076-.102 (3.0- 4.0)	>643 (698)	>643 (698)	8.4 (6.2-10.2)	1224 (902-1491)

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lap shear strengths, and below the 596 K (614°F) value of well-cured resin from this solution composition.

(5) Vacuum bag post curing for 4.3 Ks (1 1/4 hours) at 644 K (700°F) significantly increased the Tg of the adhesive in the bond line but causes a drastic reduction in the R.T. lap shear strength (Sample 12, Table 5). Visual inspection of the bond line indicated the adhesive was significantly darkened and had fractured into small particles. This is in contrast to the light color and continuous failure surfaces of the bond lines of the samples post cured at only 589 K (Samples 9, 10, and 11, Table V). TMA analysis of the adhesive bond line of one of the lap shear samples indicated a resin Tg of over 643 K (698°F) well over that for a well-cured resin of that composition (596 K, 614°F). These observations indicate that polymer degradation must have occurred during the post cure, forming a cross-linked brittle resin.

3.4 ADHESIVE CONTAINING ODA

The obvious degradation of the resin containing MPD in the bond line of lap shear specimens post cured to 644 K (700°F) indicated that either the resin was inherently less stable because of the high concentration of MPD, a potentially less stable monomer, or the NMP solvent that had not competely been eliminated from the bond line may degrade the polymer at 644 K (700°F).

To differentiate between the above two possibilities, solution composition C, Table IV, was prepared in which oxydianiline (ODA) was used in place of MPD. This adhesive solution was used to prepare adhesive prepreg, a compression molding for TMA analysis, and titanium lap shear samples.

The results of tests on lap shear samples prepared using this potentially more stable composition are given in Table VI. These lap shear samples were prepared using the procedure indicated in Section 3.1 with the exception that 1.38 MPa (200 psi) pressure was not applied during heat-up until 473 K (392°F)

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TABLE VI.

LAP SHEAR STRENGTHS AT ROOM TEMPERATURE OF POLYIMIDE BONDED 6/4 TITANIUM

Adhesive composition: 1 1/2% excess 6FTA, 60/40 PPD/ODA
Bonding conditions: 1.8 Ks (30 mins.) 589 K, full vacuum, 1.38 MPa (200 psi)
Prepreg volatile content: 9.1-9.2%

Lap Shear Sample #	Post Cure Conditions (full vacuum only)	Bond Line Thickness mm (Mils)	Resin at Bond Line		Lap Shear Strength R.T. Average of 4 (high and low)	
			Onset	Tg	MPa	psi
13	7.2 Ks (120 mins.) 589 K	-.178 (5.0-7.0)	518 K (473°F)	535 K (504°F)	32.3 (26.4-35.2)	4677 (3858-5099)
14	0.9 Ks (15 mins.) 589 K 6.3 Ks (105 mins.) 644 K 644 K	.051-.102 (2.0-4.0)	Not Tested		10.9 (0.8-13.3)	1581 (1414-1725)
15	3.6 Ks (60 mins.) 589 K 5.4 Ks (90 mins.) 616 K	.140-.178 (5.5-7.0)	503 K (446°F)	537 K (506°F)	23.6 (17.2-26.8)	3415 (2493-3893)
16	1.8 Ks (30 mins.) 589 K 1.8 Ks 602 K 1.8 Ks 616 K 1.8 Ks 631 K 1.8 Ks 644 K	.076-.102 (3.0-4.0)	Not Tested		13.5 (12.8-14.9)	1954 (1861-2155)

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was reached. The remainder of the bonding cycle was the same as that used for the samples in Table II followed by post cure conditions indicated in Table VI.

It appears that this new composition has the potential of producing higher lap shear strengths than the previous composition. Sample 13, Table VI, has an average lap shear strength at room temperature of 32.3 MPa (4677 psi) with two of the four samples having lap shear strengths over 34.5 MPa (5000 psi). These levels are well over those obtained previously - 26.20 MPa (3800 psi)[12] bonding titanium with NR-150B2G adhesive containing aluminum powder. These levels are all the more remarkable in that the failure mode is mainly adhesive. One can only guess at the lap shear strength levels obtainable when cohesive failure becomes the strength determining mode. It is believed that the strengths possible from the composition containing ODA are higher than those from the composition containing MPD because ODA produces a longer polymer chain than MPD at the same degree of polymerization (same percent excess 6FTA).

As the Tg of the resin in the bond line of Sample 13, Table V, was well below that necessary to produce acceptable lap shear strengths at 316°C, the remaining samples in Table III were processed using various post cure conditions in an effort to obtain resin in the bond line with a high Tg.

As with the samples in Table V, it was found that increasing the post cure temperature to 644 K (700°F) also resulted in a significant reduction in lap shear strength levels (Samples 14 and 16) and a significant darkening of the resin in the bond line. Some degradation in lap shear level is also indicated on post curing at 343°C (Sample 24) with little improvement in bond line resin Tg.

These results indicate that the probable cause of adhesive degradation when post curing lap shear samples at temperatures above 316°C is the interaction of the resin with the residual NMP solvent. Polymer degradation caused by the presence of residual

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NMP has also been suggested as the reason for poor mechanical properties of compression molded laminates which have not been sufficiently vented during the molding cycle[13].

3.5 POST CURING NEAT RESIN ADHESIVE BONDS: VACUUM BAG POST CURING

As the investigation in Section 3.4 indicated that post curing titanium bonded lap shear samples within the vacuum bag immediately after the bonding cycle had a complex effect on the adhesive in the bond line, this type of post cure was investigated further. Lap shear samples using 6/4 titanium coupons were bonded four-at-a-time using the simulated autoclave conditions in a press as indicated in Section 3.1 with the exception that the application of 1.38 MPa (200 psi) pressure was delayed until 473 K (392°F) was reached during heat-up and the time and temperature of the post cure while under full vacuum and zero pressure was varied. Lap shear samples were bonded using either adhesive prepreg based on solution composition A, Table IV (containing MPD) or solution composition C, Table IV (containing ODA). The results of this study are shown in Table VII, in which the vacuum post cure conditions, the onset temperature (O.T.), and Tg of the resin at the bond line, and the lap shear strengths at either R.T. or 589 K are given.

Conclusions obtained from the data in Table VII are as follows:

(1) Post curing under vacuum for 10.8 Ks (3 hours) at 589 K does not give acceptable 589 K lap shear strengths using either of the adhesive solution compositions (see Samples 20 and 24, Table VII).

(2) Using adhesive composition A (MPD comonomer), increasing the post cure time from 3.6 Ks (1 hour) to 10.8 Ks (3 hours) and to 72.0 Ks (20 hours) results in a regular decrease in R.T. bond strength with the strength after the 72.0 Ks post cure severely degraded (Samples 17, 18, 19, and 21, Table VII).

TABLE VII.

EFFECT OF POST CURE IN VACUUM BAG ON PROPERTIES OF POLYIMIDE BONDED 6/4 TITANIUM

Adhesive Composition: 1-1/2% excess 6FTA*, 60/40 PPD*/Codiamine
Adhesive Prepreg Volatile Content ~10%
Bonding Conditions: (30 mins.-1.8 Ks), 589 K full vacuum, 1.38 MPa (200 psi)

Sample #	Comonomer In Adhesive	Post Cure Conditions Full Vacuum, Zero Pressure Time Ks (Hours)	Temp. K (°F)	Resin At Bond Line O.T. K (°F)	Tg K (°F)	Lap Shear Strength (Average of 4) R.T. MPa (psi)	589 K MPa (psi)
17	MPD* (Solution A)	3.6 (1)	589 (600)	498 (437)	508 (455)	24.10 (3490)	
18	"	10.8 (3)	"		553 (536)	18.96 (2750)	
19	"	10.8 (3)	"	573 (572)	578 (582)	18.30 (2654)	
20	"	10.8 (3)	"	528 (492)	578 (582)		0.54 (79)
21	"	72.0 (20)			565 (558)	13.32 (1932)	
22	ODA* (Solution B)	7.2 (2)	589 (600)	518 (473)	535 (504)	32.30 (4677)	
23	"	7.2 (3)	"	498 (237)	520 (476)	31.52 (4572)	
24	"	7.2 (3)	"	553 (536)	571 (568)		1.19 (172)
25	"	0.9 (1/4) 6.3(1 3/4)	589 644 } (600 700){ 644 (700)	553 (536)	553 (536)	10.90 (1581)	

*6FTA: 2,2 bis (3',4'-dicarboxyphenyl) hexafluoropropane
PPD: paraphenylenediamine
MPD: metaphenylenediamine
ODA: oxydianiline

(3)   Using adhesive composition C (ODA comonomer), the R.T. lap shear strength remains at high levels on post curing for 7.2 Ks (2 hours) or 10.8 Ks (3 hours) (Samples 22 and 23, Table VII).

(4)   Post curing in a vacuum bag, samples prepared using composition C (ODA comonomer) for 6.3 Ks (1 3/4 hours) at 644 K (700°F) also severely degrades the R.T. lap shear strength (Sample 25, Table VII).

(5)   With either adhesive composition, increasing the post cure time or temperature while under full vacuum does not increase the Tg of the adhesive at the bond line to the desired 589 K or above temperature.

3.6   TMA ANALYSIS OF BOND LINE ADHESIVE

The onset temperature (O.T.) and glass transition temperature (Tg) of the bond line adhesive of all of the samples in Table VII have been measured using the thermomechanical analysis method.   A small sample of adhesive/metal laminate, cut from the failed lap shear sample, is analyzed.   As the titanium shows little dimensional change over the temperature range investigated, the TMA curves obtained are characteristic of the adhesive.   TMA curves for Samples 19, 20, 24, and 25, Table VII, are presented in Figures 3, 4, 5, and 6.   Although the bond line adhesive in Samples 19 and 20 (Figures 3 and 4) show the same Tg (578 K), the shapes of the curve indicate that the adhesive in Sample 19 has a higher degree of cure (lower levels of NMP remaining) than Sample 20.

The TMA curves shown in Figures 5 and 6 (Samples 24 and 25) do not indicate unequivocally the Tg of these samples.   There may be some cross-linking occurring which may complicate the curve.   Only the determination of 589 K lap shear strengths will determine the quality of these samples.

FIGURE 3
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 19 TABLE VII
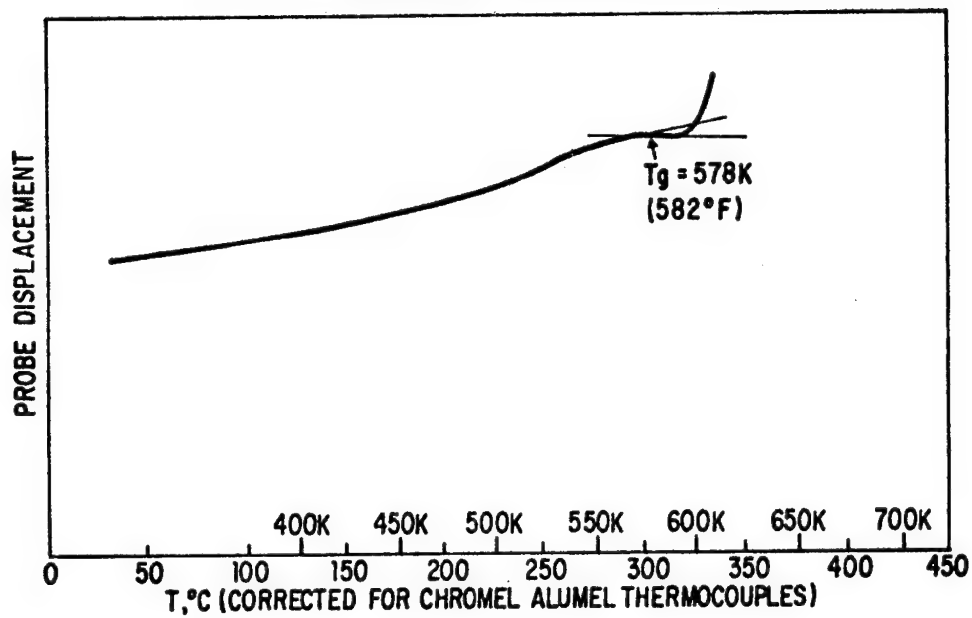
FIGURE 4
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 20 TABLE VII

FIGURE 5
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 24 TABLE VII

Tg = 571K
(568°F)

O.T. = 553K
(536°F)

PROBE DISPLACEMENT

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450

T,°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

FIGURE 6
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 25 TABLE VII

Tg = 553K
(536°F)

PROBE DISPLACEMENT

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450

T,°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

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3.7 FREE STANDING AIR POST CURE

The data in Table VII indicate that a post cure within the vacuum bag produces an adhesive bond line with a Tg below the desired 589 K (600°F) and decreases the R.T. lap shear strength. As the attainment of acceptable lap shear strengths at both R.T. and 589 K could not be easily obtained by this post cure method, its investigation was abandoned, and the use of a free standing air post cure was evaluated. Lap shear samples were first post cured at 589 K in the vacuum bag to ensure low volatile levels in the bond line, then cooled, removed from the bag assembly, and post cured in air using a small laboratory oven.

The results of using this method of post curing are given in Table VIII. The post cure conditions used in the vacuum bag and in air are indicated as well as the effect of these conditions on the bond line resin Tg, the change in the bond line thickness after air post cure, and the lap shear atrength. In all cases in the Table, the bond line thickness and the percent increase are the average of the four samples bonded at one time. The air post cure was carried out by increasing linearly the oven temperature to the final temperature over the entire time period indicated.

The following conclusions are noted from the data in Table VIII:

(1) Post curing in air reduces the R.T. lap shear strength but increases the 316°C lap shear strength with either adhesive composition evaluated. (Compare Samples 26 and 27, Table VIII, with Samples 19 and 20, Table VII and Samples 32 and 33, Table VIII with Samples 23 and 24, Table VII.)

(2) The bond line significantly increases in thickness (swells) on post curing free standing in air.

(3) The tendency for the bond line to swell on post curing in air can be reduced by (1) increasing the time of the vacuum post cure at 589 K and (2) starting the air post cure at a temperature well below the Tg of the resin at the bond line after the vacuum post cure (compare Samples 30 and 31 with Samples 32

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TABLE VIII.

EFFECT OF POST CURE IN AIR ON PROPERTIES OF
POLYIMIDE BONDED 6/4 TITANIUM LAP SHEAR SAMPLES

Adhesive Composition: 1-1/2% excess 6FTA*, 60/40 PPD*/Codiamine
Adhesive Prepreg Volatile Content ~10%
Bonding Conditions: (30 mins.-1.8 Ks), 589 K (600°F) full vacuum
                 1.38 MPa (200 psi)

| | | Post Cure Conditions | | | | Resin at Bond Line | | Bond Line Thickness | | Lap Shear Strength (Average of 4) | |
| | | First, Full Vacuum No Pressure | | Followed By Air Oven | | | | | | | |
Sample #	Comonomer In Adhesive	Time Ks (Hours)	Temp. K (°F)	Time Ks (Hours)	Temp. K (°F)	Onset Temp. K (°F)	Tg °C K (°F)	Average Before Air Post Cure	% Increase After Air Post Cure	@ R.T. MPa (psi)	@ 589 K MPa (psi)
26	MPD*	10.8 (3)	589 (600)	81.0 (22-1/2)	530→644 (495) (600)	—	583 (590)	.191 mm (7.5 mils)	51%	10.36 (1503)	
27	"	10.8 (3)	"	"	"	Not Tested		.152 mm (6.0 mils)	57%		6.68 (969)
28	ODA*	1.8 (1/2)	589 (600)	82.8 (23)	494→644 (430) (600)	588 (598)	593 (608)	.155 mm (6.1 mils)	44%	18.24 (2646)	
29	"	1.8 (1/2)	"	"	"	Not Tested		.137 mm (5.4 mils)	46%		5.27 (765)
30	ODA	3.6 (1)	589 (600)	81.0 (22-1/2)	530→644 (495) (600)	573 (572)	590 (602)	.135 mm (5.3 mils)	57%	17.46 (2532)	
31	"	3.6 (1)	"	"	"	Not Tested		.152 mm (6.0 mils)	90%		5.05 (733)
32	ODA	10.8 (3)	589 (600)	86.4 (24)	473→644 (392) (600)	563 (554)	575 (576)	.147 mm (5.8 mils)	42%	18.23 (2644)	
33	"	10.8 (3)	"	"	"	~593 (608)	596 (614)	.140 mm (5.5 mils)	27%		8.47 (1288)

*6FTA: 2,2 bis (3',4'-dicarboxyphenyl) hexafluoropropane
PPD: paraphenylenediamine
MPD: metaphenylenediamine
ODA: oxydianiline

and 33, Table VIII).

(4) Post curing in air increases the Tg of the adhesive
resin in the bond line in some cases to the desired level,
e.g., ≥589 K (600°F).

Many of the lap shear samples which have been air post cured
fail cohesively within the adhesive bond line. It is believed that
this type of failure is caused by the presence of volatiles which
swell the bond line on post cure producing a porous weak bond. As
the Tg of the bond line adhesive of some of the samples in Table
VIII is above 589 K, the 589 K lap shear sample should be at
higher levels than observed. A significant reduction in the bond
line swelling must be made, therefore, before acceptable lap shear
bond strengths will be realized at both R.T. and 589 K.

The curves from the TMA analysis for Samples 26, 28, 30, and
33, Table VIII are shown in Figures 7, 8, 9, and 10.

3.8 AIR POST CURING UNDER PRESSURE

In order to reduce the swelling of the bond line, lap shear
samples prepared using NMP based adhesive solutions were air post
cured while the bond lines were under pressure as indicated below.

Four lap shear samples (made using the 4 gang 6/4 titanium
coupons) were bonded and vacuum post cured for four hours using
the procedure indicated in Section 3.5 with neat resin adhesive
prepreg. The lap shear samples were then post cured in air under
a 0.14 MPa (20 psi) pressure using a press while increasing the
temperature linearly from 418 K (393°F) to 661 K (730°F) over a
129.6 KS (36 hour) period. These four samples exhibited an
average bond line swelling of only 11% with the individual values
varying from 8% to 18% and an average 589 K lap shear strength of
10.43 MPa (1512 psi) with the values varying from 9.64 MPa (1398
psi) to 11.98 MPa (1737 psi). Thus, by reducing the bond line
swelling, higher and more controlled 589 K lap shear strengths
can be obtained with a prepreg based on neat resin.

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FIGURE 7
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 26 TABLE VIII

Tg = 583 K
(590°F)

PROBE DISPLACEMENT

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450

T,°C(CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)
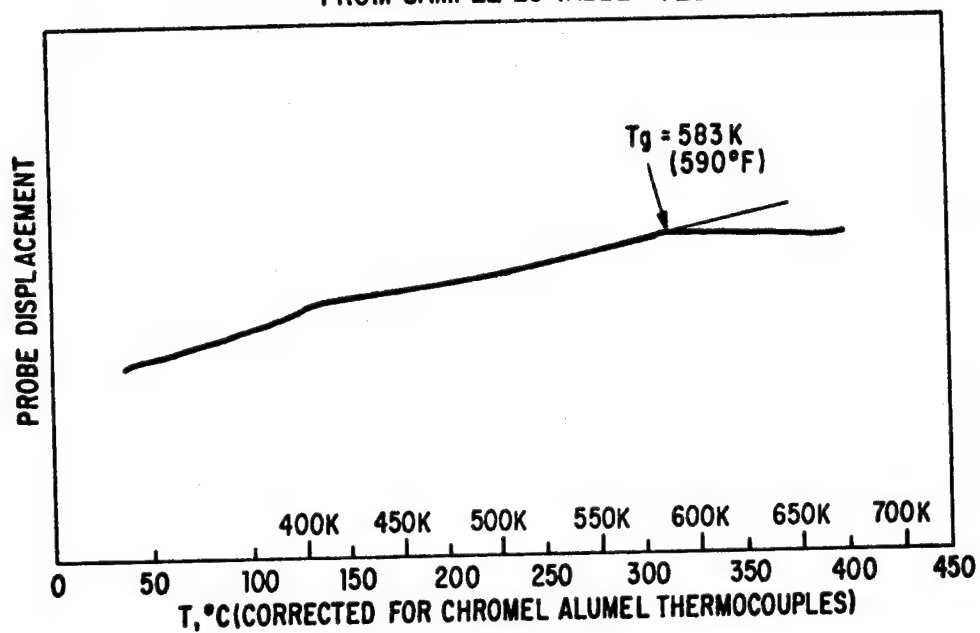
FIGURE 8
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 28 TABLE VIII

Tg = 593K
(608°F)

PROBE DISPLACEMENT

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450

T,°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)
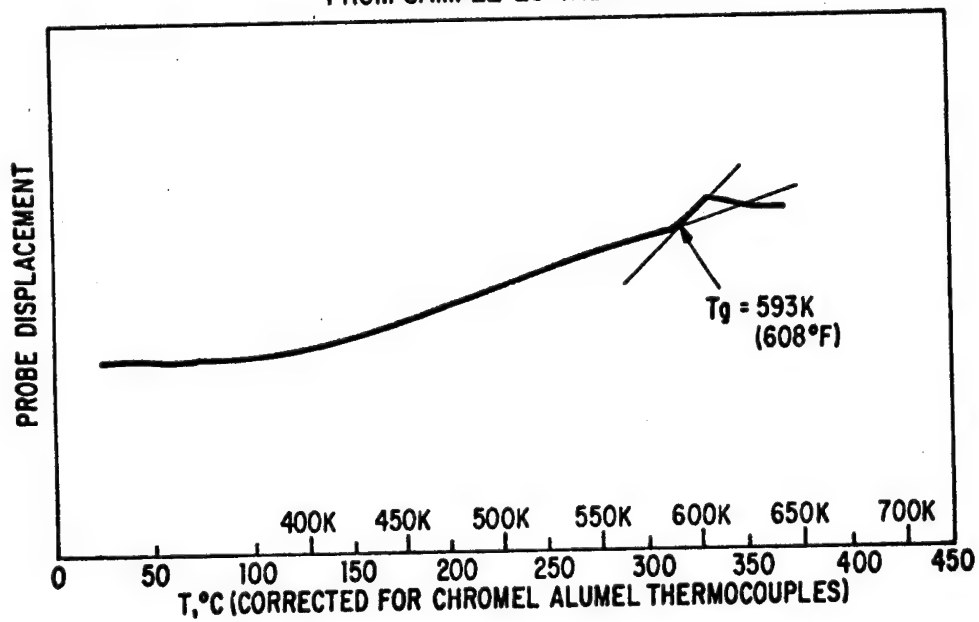
FIGURE 9
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 30 TABLE VIII
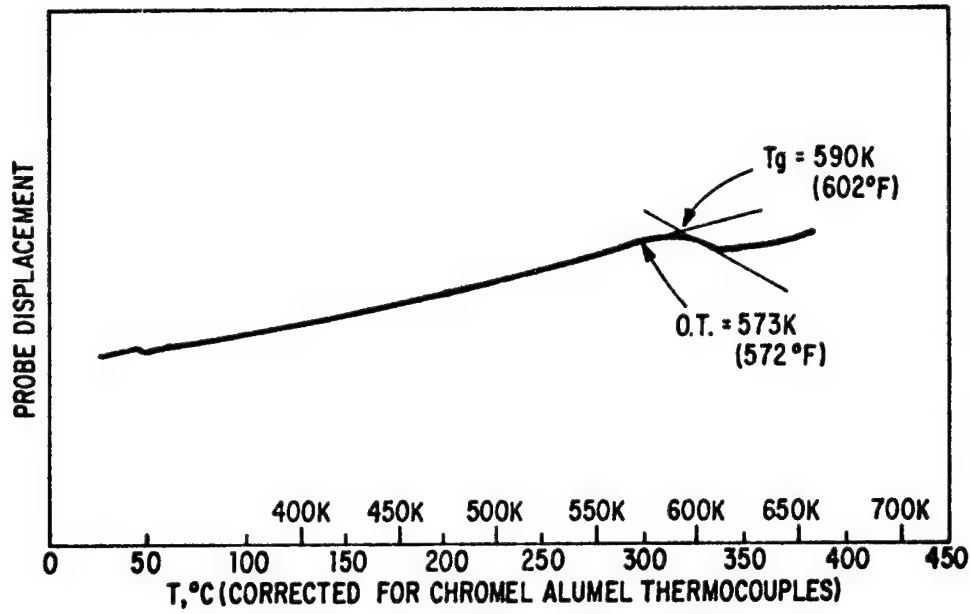
FIGURE 10
TMA CURVE OF
ADHESIVE BOND LINE
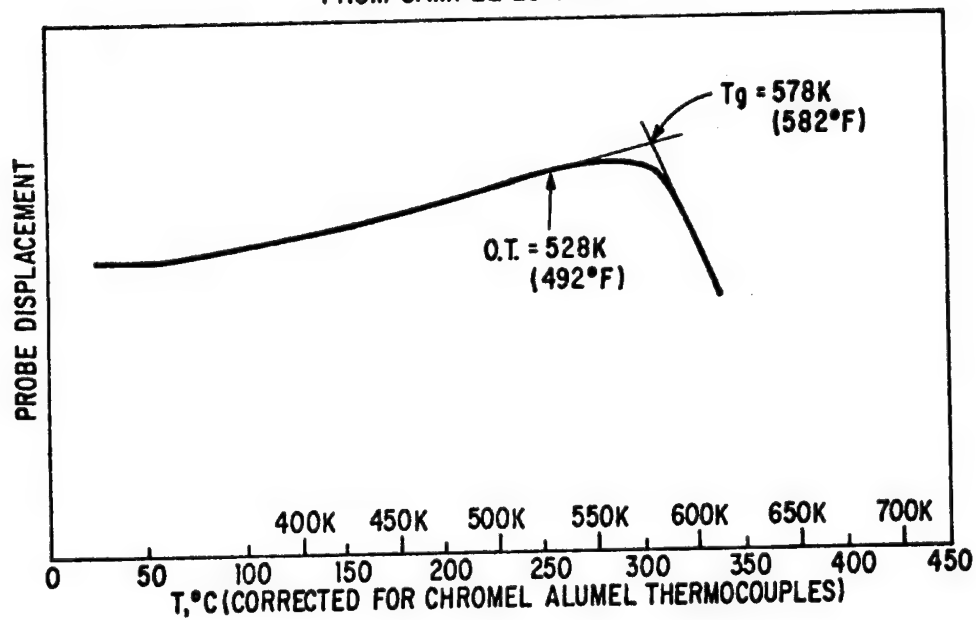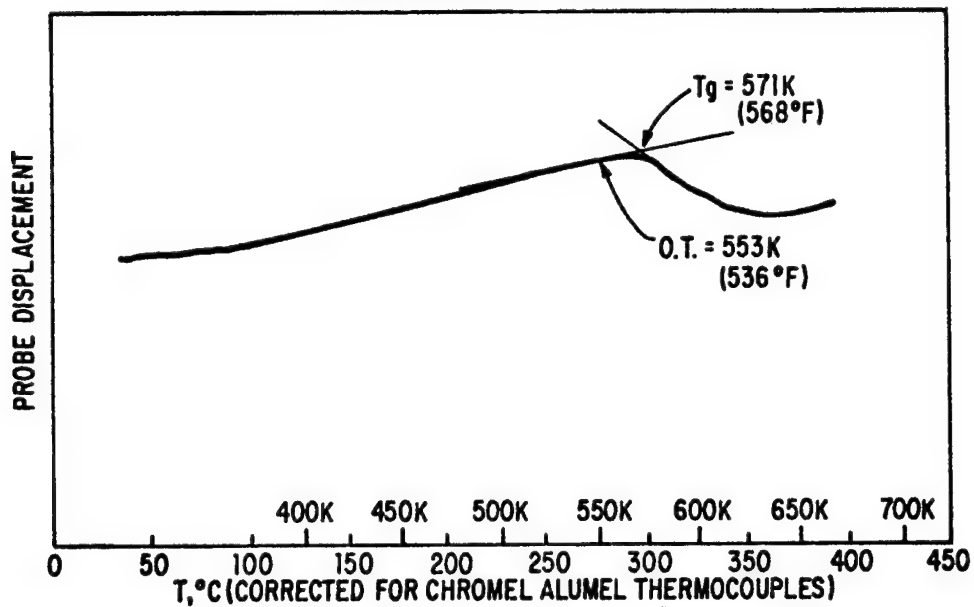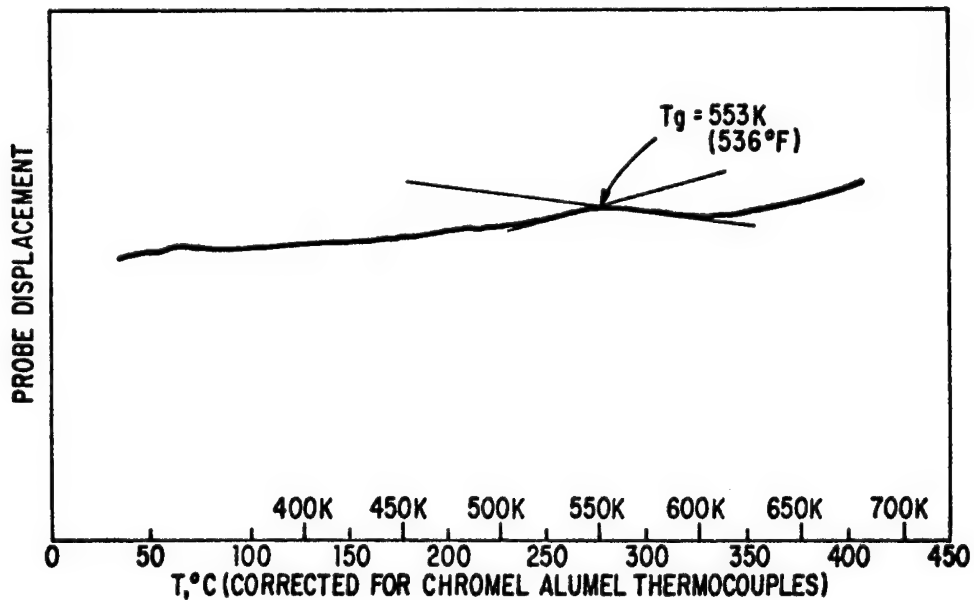FROM SAMPLE 33 TABLE VIII
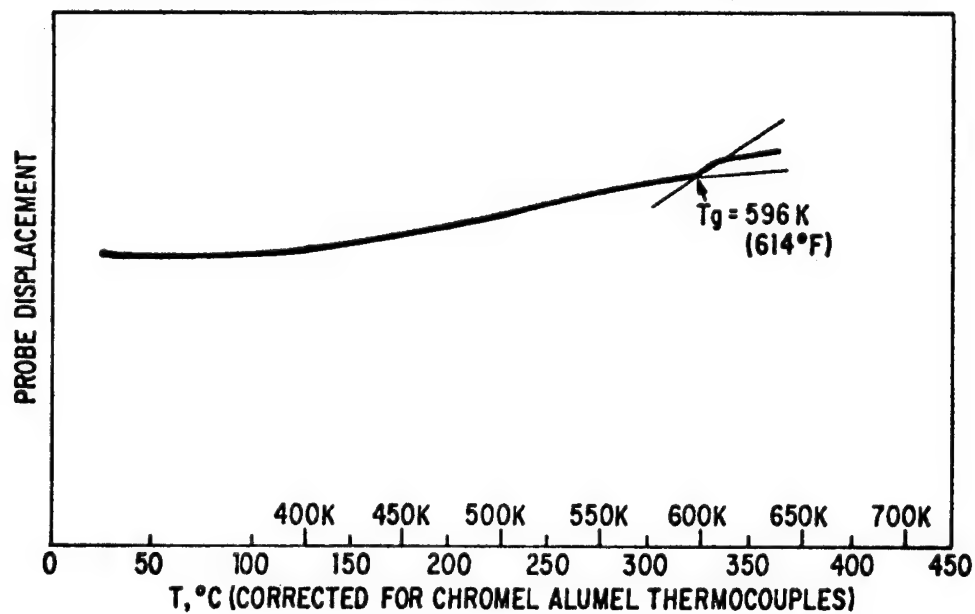
4.   ALUMINUM POWDER FILLED ADHESIVE COMPOSITIONS

The work on developing a process for bonding titanium using unfilled adhesive prepreg based on NR-150 polyimide precursor solutions containing NMP solvent indicated that a complex air post cure step would probably be required to produce acceptable lap shear bonds at both R.T. and 589 K (600°F). It was apparent, therefore, that the objective of developing a more easily processed adhesive would not be met using this system.

As NASA had recently determined that there were no deleterious effects on bonding graphite fiber composites with aluminum powder filled adhesives, the work was directed toward evaluating NR-150 adhesive solution containing aluminum. A filler such as aluminum powder would be expected to increase the Tg of the adhesive bond line and reduce bond line swelling during post cure.

4.1   INITIAL EXPERIMENTS

The initial work on this second task concerned the evaluation of adhesive prepreg based on adhesive solution C, Table IV, containing 35 wt. % aluminum powder based on total cured solids. The aluminum powder used in this study was Reynolds Grade 1-131 atomized powder having a particle size of about .01 mm (10 microns). The adhesive solution containing the aluminum powder was used to prepare the adhesive prepreg as well as to prime the etched titanium surface. The procedures indicated in Appendices A and B were used for this study. The adhesive prepreg was prepared as indicated in Section 3.1 and "B" staged at 418 K (293°F) only. The volatile content was controlled by the staging time. Adhesive prepreg .279 mm (11 mils) thick prepared from this solution using 112 Style E glass with a volatiles content of 14.3% has a unit weight of .0187 Kg/m^2 (.09 lbs./ft^2) and contains 48 wt. % cured resin solids, 21 wt. % aluminum powder, and 17 wt. % glass scrim cloth.

The initial experiments defined the volatile content of the prepreg required to give acceptable R.T. bond strengths. Lap shear strengths of bonds produced using adhesive prepreg containing aluminum powder are shown in Table IX. Also indicated are the:

TABLE IX.

6/4 TITANIUM LAP SHEAR SAMPLES BONDED WITH ALUMINUM-FILLED EXPERIMENTAL NR-150 ADHESIVE PREPREG

ADHESIVE SOLUTION COMPOSITION: 1-1/2% EXCESS 6FTA, 60/40 PPD/ODA, 35 WT. % REYNOLDS ALUMINUM POWDER GRADE 1-131

BONDING CONDITIONS: HEAT-UP RATE ~.047 K/SEC. (2°C/MIN.) FULL VACUUM 1.38 MPa (200 psi)
HOLD 1.8 Ks (30 MINS.) FULL VACUUM 1.38 MPa (200 psi)

Lap Shear Sample #	Volatiles Content %	Bond Line Thickness mm (mils)	Squeeze Out At Bond Line	Primer Coating Thickness mm (mils)	Post Cure Time at 589 K Vacuum Ks (Hours)	Lap Shear Strength (Average of 4) R.T. MPa (psi)	Lap Shear Strength (Average of 4) 316°C MPa (psi)	Remarks Type Failure
34	11.9	.203 (8)	Very Little	<.0254 (<1.0)	3.6 (1)	13.94 (2029)		Adhesive (Poor Flow)
35	"	.18 (7)	"	<.0254 (<1.0)	"		1.43 (207)	"
36	12.8	.203 (8)	Very Little	<.0254 (<1.0)	3.6 (1)	12.78 (1854)		Adhesive (Poor Flow)
37	"	.19 (7-1/2)	"	"	"		1.71 (248)	"
38	13.5	.14 (5-1/2)	Slight	<.0254 (<1.0)	3.6 (1)	24.48 (3551)		Some Cohesive Failure
39	"	.165 (6-1/2)	"	"	"		1.08 (156)	80% Cohesive Failure
40	14.0	.114 (4-1/2)	Moderate	<.0254 (<1.0)	14.4 (4)	18.60 (2697)		Fabric to Resin Failure Some Cohesive Failure
41	"	.076 (3)	"	"	"		3.05 (442)	Fabric to Resin Failure High Value = 9.17 (1330)
42	15.4	.076 (3)	Good	<.0254 (<1.0)	14.4 (4)	18.05 (2618)		Fabric to Resin & Cohesive
43	"	.09 (3-1/2)	"	"	"		2.44 (352)	Fabric to Resin Failure High Value = 7.37 (1070)
44	12.5	.063 (2-1/2)	Excessive	.051-.076 (2.0-3.0)	3.6 (1)	24.27 (3520)		Fabric to Resin Failure
45	"	.076 (3)	"	"	"		1.15 (167)	"

prepreg volatile content, bond line thickness, primer coating
thickness, post cure time at 589 K under vacuum, resin squeeze
out at the bond line, and the type of lap shear failure that
occurred during testing.

From the data in Table VIII, it can be seen that an adhesive
prepreg volatile content of about 13.5 wt. % is optimum, giving
an average R.T. lap shear strength of 24.48 MPa (3551 psi)
(Sample 38, Table VIII). However, if the titanium adherend primer
coating thickness is increased from less than .0254 mm (1 mil) to
.051-.076 (2-3 mils), then an adhesive prepreg volatile content
of about 12.5 wt. % will also give high R.T. lap shear levels of
24.27 MPa (3520 psi) (see Sample 44, Table IX). These higher
prepreg volatile content levels are to be contrasted with a level
of about 10% required for prepreg based on neat (unfilled) resin
systems (see Tables VII and VIII).

Using adhesive prepreg with a volatile content greater than
13.5%, lower R.T. lap shear strengths occur because the adhesive
bond line becomes too thin. Poorer lap shear strengths result
because of a resin starved bond which then fails at the glass
scrim cloth/resin interface.

4.2 EFFECT OF FILLER CONCENTRATION

The effect of aluminum powder loadings of 35, 50, and 65 wt.
% (based on total cured solids) in the adhesive solution was
investigated. For this work, the following adhesive solution
composition was used:

ADHESIVE SOLUTION D

Composition	Onset Temp. of Molding	Tg of Molding
1:1 6FTA:diamine 60/40 PPD/ODA 48 wt. % cured resin solids in NMP.	None	605 K (630°F)

This new adhesive solution composition was picked for three reasons:

First, prepreg based on Solution D has a resin flow qualitatively equivalent to that for Solution C prepreg at the same volatiles content.

Second, well-cured resin from Solution D has a Tg (332°C), somewhat above that from Solution C (321°C). It should be easier, therefore, to obtain bond lines having a Tg above 316°C with Solution D than with Solution C.

Third, at the same aluminum powder loading and "B" stage condition, this composition produces tougher prepreg than the previous composition. It would be expected that at high aluminum powder loadings the adhesive composition producing a higher molecular weight would produce tougher more resilient adhesive bonds. The relationship of the Tg of this well-cured resin to the previously evaluated resin compositions and the commercial NR-150B2G (1:1 6FTA:diamine, 95/5 PPD/MPD) is given in Figure 1.

4.2.1 Control of Bond Line Thickness

In the initial experiments, it was found that the addition of aluminum powder significantly reduced the resin flow in the bond line as compared to neat resin. As a result, prepreg containing aluminum powder is "B" staged using more mild conditions, thereby reducing the degree of resin cure (a higher volatiles content).

Use of prepreg having resin with a lower degree of cure makes control of the bond line thickness more difficult. Prepreg with resin having a lower degree of cure is less forgiving and requires greater precision in processing. Too thin a bond line is usually obtained. With too thin a bond line, the resin has been squeezed out from around the carrier cloth, giving a resin starved bond line resulting in poor lap shear strengths which fail at the glass-resin interface.

In order to prevent this problem, two changes were made in the procedures used: First, the primer coating thickness was increased from below .025 mm (1.0 mil) to .050 to .075 mm (2.0-

3.0 mils). The primer coating was "B" staged 5 minutes at 418 K (293°F) as before. Increasing the primer coating thickness without changing the primer "B" stage conditions results in a coating having a lower degree of cure and permits the use of prepreg with a lower volatile content.

Second, the adhesive prepreg was prepared by a double coating process in which a thin coat of solution was applied to the glass scrim carrier cloth and "B" staged to ensure the resin near the glass cloth was well cured. A second coating was then applied and "B" staged to a lesser extent than the first coating. The glass cloth is about .089 mm (3.5 mils) thick; the first coating is about .178 mm (7.0 mils) thick; and the final coating results in a prepreg total thickness of .279-.381 mm (11-15 mils). The final thickness of the prepreg, therefore, was similar to that prepared using the single coat process as described in Section 3.1.

4.2.2 Lap Shear Strengths of Filled Adhesive Bonds

The bond strengths of lap shear samples from titanium adherends bonded with adhesive containing 35, 50, and 65 wt. % aluminum powder (based on total cured solids) are given in Table X. For this evaluation, two sets of four simultaneous bondings were made resulting in eight samples, four of which were tested at R.T. and four at 589 K (600°F). The adhesive prepreg was made by coating 112 Style E glass (I-589 finish) two successive times, "B" staging after each coating. The "B" stage conditions used, prepreg thickness and volatiles content, lap shear bond line thickness, and amount of squeeze out at bond line are all indicated in Table X.

The data presented in Table X can be summarized as follows:

(1) Increasing the concentration of aluminum powder filler requires a reduction in the time and/or temperature of "B" staging to obtain the same prepreg volatiles content.

(2) High R.T. lap shear strength levels are obtained with prepreg having a volatiles content of about 7 1/2%, a volatiles level lower than that found necessary using unfilled adhesive as

TABLE X.

LAP SHEAR STRENGTHS OF 6/4 TITANIUM
BONDED WITH EXPERIMENTAL NR-150 ADHESIVE
CONTAINING ALUMINUM POWDER

Adhesive Solution Composition: 1:1 6FTA[1]:Diamine, 60/40 PPD/ODA, 48 wt. % in NMP[1]

1	2	3	4	5	6	7	8	9	10	11
Lap Shear Sample #	Aluminum Powder Concentration %[2]	Prepreg "B" Stage Conditions-Two Successive Coatings 1) After First Coating 2) After Second Coating	Volatiles in Prepreg %	Bond Line Thickness mm (Mils)	Squeeze Out at Bond Line	Lap Shear Strength (Average of 4) (High and Low Values) MPa (psi) R.T.	589K(600°F)	Failure Mode	O.T. Measured on Failed Bond Line K	Tg Measured on Failed Bond Line K
46	35	1) 1.8 Ks(30 min) 418K(293°F); 3.6 Ks(60 min) 418K(293°F) 2) 1.8 Ks(30 min) 433K(320°F)	10	.051-.127 (2.0-5.0)	Excessive	25.15(3647) 18.8-30.8		Adhesive	265	280
47	"	1) 1.8 Ks(30 min) 418K(293°F); 0.9 Ks(15 min) 433K(320°F) 2) 1.8 Ks(30 min) 418K(293°F); 2.7 Ks(45 min) 433K(320°F)	"				1.36(197) 11.25-1.44	Fabric/Resin		302
48	"		9.0	.038-.127 (1.5-5.0)	Moderate to Excessive	29.14(4226) 27.7-30.5		Fabric/Resin	287	
49			"				1.27(184) 1.01-1.48	Fabric/Resin		
50	"	1) 1.8 Ks(30 min) 418K(293°F); 3.6 Ks(30 min) 433K(320°F) 2) 3.6 Ks(60 min) 418K(293°F); 1.8 Ks(30 min) 433K(320°F)	7.6	.114-.216 (4.5-8.5)	Moderate	30.48(4420) 29.1-31.5		Adhesive	280	285
51		1.8 Ks(30 min) 448K(347°F)						Fabric/Resin and Cohesive		
52	50	1) 1.8 Ks(30 min) 418K(293°F); 2.4 Ks(40 min) 418K(293°F) 2) 1.8 Ks(30 min) 433K(320°F)	8.8	.051-.085 (2.0-3.5)	Excessive	20.87(3027) 17.9-23.1	1.25(181) 0.84-1.62	Fabric/Resin		300
53	"		"		"			"		
54	"	1) 1.8 Ks(30 min) 418K(293°F); 1.2 Ks(20 min) 433K(320°F) 2) 3.6 Ks(60 min) 418K(293°F); 3.6 Ks(60 min) 433K(320°F)	6.9	.152-.279 (6.0-11.0)	Moderate	23.75(3445) 20.5-26.2	0.96(139) 0.81-1.27	Adhesive	290	312
55	"		"		"		1.61(233) 1.0-1.8	Cohesive		
56	65	1) 1.2 Ks(20 min) 418K(293°F); 0.6 Ks(10 min) 433K(320°F) 2) 1.8 Ks(30 min) 418K(293°F)	7.5	.140-.203 (5.5-8.0)	Slight	29.85(4326) 23.9-36.87 (Average of 3)	1.74(253) (Average of 3)	Adhesive-Cohesive	310[4]	322[4]
57	"		"		Moderate			Cohesive Cohesive		

[1] 6FTA = 2,2 bis(3',4'-dicarboxyphenyl) hexafluoropropane; PPD = paraphenylenediamine; ODA = oxydianiline; NMP = N-methylpyrrolidone

[2] concentration based on total cured solids

[3] bonding conditions: R.T. to 473 K (392°F), full vacuum at .033 K/sec (3.6°F/min); 473 K to 589 K full vacuum, 1.38 MPa (200 psi) at 589 K; post cure 14.4 Ks (4 hrs.), 589 K, full vacuum

[4] measured on the titanium/adhesive/titanium sandwich cut from an untested lap shear sample

indicated in Table VI. This lower volatile content is possible because of: (1) the thicker primer coating on the titanium adherends as compared to that used previously (.0254-.0508 mm, 1-2 mils vs ~.0127 mm, 0-5 mils), and (2) the use of prepreg coated two successive times with, therefore, better control of the resin cure near the glass scrim carrier.

(3) Use of 65 wt. % concentration of aluminum powder filler in the adhesive does not degrade the R.T. lap shear strengths. The average lap shear strength of 29.85 MPa (4326 psi) for Sample 56 containing 65 wt. % filler compares favorably with the strength of 30.48 MPa (4420 psi) for Sample 50 containing 35 wt. % filler (Table X).

In fact, one lap shear specimen of the three tested of Sample 57 had a bond strength of 36.87 MPa (5347 psi), the highest R.T. lap shear strength obtained in this program.

(4) Surprisingly, under the bonding conditions used as indicated in footnote 3, Table X, there was no improvement in the 589 K (600°F) lap shear strength on increasing the aluminum powder filler concentration in the adhesive. With all samples tested, the 589 K strengths were very low and all failures were cohesive in the adhesive layer.

(5) Increasing the aluminum powder filler concentration in the adhesive increases the Tg of the resin in the bond line. At a 65 wt. % aluminum powder concentration, the Tg of the adhesive resin in the bond line is 595 K (612°F), above the 589 K test temperature; but the onset temperature (O.T.) was below the test temperature. It can only be concluded that acceptable 589 K bond strengths will be attained only when the adhesive resin in the bond line has both the O.T. and Tg above 589 K.

4.3 POST CURING ALUMINUM-FILLED ADHESIVE BONDS

Lap shear samples prepared using titanium adherends and aluminum powder filled adhesive solutions have been post cured free standing in air at various temperatures. These samples were prepared using several adhesive solution compositions with several

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aluminum powder filler concentrations. The titanium adherends
were surface etched and primed using procedures in Appendix A and
Appendix B, Part I. The adhesive prepreg was prepared using the
double coating process indicated in Appendix D. Three adhesive
solution compositions were evaluated: Composition D (Section 4.2)
containing 65 wt. % aluminum powder filler; a solution containing
a 25/25 ratio of PPD/ODA with 60% filler, and NR-150B2G adhesive
solution containing 60% filler. All of the solutions had a con-
centration of 48 wt. % cured resin solids in NMP. The solutions
containing aluminum powder were used to prime the titanium adherend
surface as well as to prepare prepreg.

The lap shear strengths of samples post cured in air are
reported in Table XI. The bonding cycle used for these samples is
given at the bottom of Table XI with the time for post curing in
the vacuum bag indicated in Column 7. As shown in Column 8 and 9,
air post cures of 28.8-57.6 Ks (8-16 hours) at temperatures of
589-644 K (600-700°F) were used.

The results of this post cure study are summarized as follows:

(1) Constant temperature post cure, free standing in air
increases the 589 K lap shear strengths, but decreases the R.T.
lap shear strengths (compare Samples 60 and 61 with Samples 58 and
59, Table XI).

(2) No improvement in the 589 K bond strength is observed
on post curing at 616 K (650°F) as compared to post curing at
589 K (600°F) (compare Samples 64 and 65 with 60 and 61, Table
XI).

(3) Samples bonded with adhesive from solution Composition
D (60/40 PPD/ODA) which are post cured to 644 K (700°F) show a
dramatic improvement in the 589 K bond strength (Samples 66 and 67,
Table XI).

TABLE XI.

EFFECT OF ISOTHERMAL AIR POST CURE ON LAP SHEAR STRENGTHS
OF 6/4 TITANIUM BONDED WITH NR-150 ADHESIVE COMPOSITIONS

1	2	3	4	5	6	7	8	9	10	11	12	13
Lap Shear Sample #	Diamines Used and Ratio	Al Powder Content %	Tg of Well Cured Resin K (°F)	Prepreg Volatile Content %	Resin Squeeze-Out on Bonding	Vacuum Post Cure K (Hours) at 589 K(600°F)	Air Post Cure Time Ks (Hrs.)	Air Post Cure Temp. K (°F)	Lap Shear Strength [ ] No. of Samples (High and Low Values) at R.T. MPa (psi)	Lap Shear Strength [ ] No. of Samples (High and Low Values) at 589 K(600°F) MPa (psi)	Resin at Bond Line Onset Temp. K(°F)	Resin at Bond Line Tg K(°F)
58	PPD*/ODA* 60/40	65	605(630)	7.6	Good	14.4 (4)	None	None	30.48(4420)[4] (29.10-31.11)		553 (536)	558 (545)
59		"	"	"	"	"				1.25(181)[4] (.84-1.61)		
60	PPD/ODA 60/40	65	605(630)	7.7	Good	14.4 (4)	57.6 (16)	589 (600)	16.48(2390)[3] (14.82-17.77)		548 (527)	571 (568)
61					"	"				4.94(716)[4] (3.74-6.19)		
62	"	"	"	9.2	"	3.6 (1)	"	589 (600)	19.48(2825)[3] (16.78-21.29)		573 (572)	580 (585)
63		"	"	"	"	"				6.79(985)[4]	573	590
64	PPD/ODA 60/40	65	605(630)	8.5	Slight	3.6 (1)	28.8 (8)	589 (600)	14.38(2085)[3]			
65		"	"	"	"	"	57.6 (16)	616 (650)		5.41(785)[4] (4.76-6.01)		
66	PPD/ODA	65	605(630)	9.0	Good	3.6 (1)	57.6 (16) / 28.8 (8) / 28.8 (8) / 57.6 (16)	589 (600) / 616 (650) / 644 (700)	14.21(2061)[1]	9.22(1337)[2] (8.98-9.46)	595 (612)	595 (612)
67	"	"	"	"	"	"	"	"	11.20(1624)[1]	9.61(1394)[2] (8.34-10.83)	593 (608)	593
68	PPD/ODA 75/25	60	613(644)	9.7	Slight	3.6 (1)	57.6 (16)	589 (600)	19.25(2792)[3] (15.83-21.14)		593 (608)	600 (620)
69	"	"	"	10.4	Good	"	28.8 (8)	589 (600)	14.15(2052)[3] (12.47-15.69)		583 (590)	593 (608)
70	"	"	"	"	"	"	57.6 (16)	616 (650)		6.06(879)[4] (4.85-7.03)		
71	"	"	"	"	"	"				8.72(1265)[4] (6.96-11.35)		
72	PPD/MPD* 95/5	60	633(680)	11.7	Slight	3.6 (1)	None	None	15.74(2283)[3] (13.35-17.01)		518 (474)	565 (558)
73		"	"	"	"	"				2.44(354)[4] (1.26-4.32)		

Bonding Conditions: Heat samples at 2 K/min. from R.T. to 573 K (200°F) under full vacuum; heat 573 K to 589 K (600°F) at 2 K/min. under full vacuum and 1.38 MPa (200 psi); bond 1/2 hour at 589 K (600°F), full vacuum, 1.38 MPa (200 psi)

*PPD = paraphenylenediamine; ODA = oxydianiline; MPD = metaphenylenediamine
All adhesive solution compositions contain 1:1 ratio of tetraacid to diamine

(4) Lap shear samples based on the 75/25 PPD/ODA adhesive composition post cured at 616 K (650°F) have bond strengths similar to samples based on adhesive Composition D (60/40 PPD/ODA) post cured to 644 K (700°F) (compare Samples 70 and 71 with Samples 66 and 67, Table XI).

(5) Lap shear samples bonded with aluminum powder filled NR-150B2G adhesive solution will also require an air post cure to give high 589 K bond strengths (Samples 72 and 73, Table XI).

(6) Although three of the lap shear samples analyzed by the TMA technique showed the adhesive in the bond line to have both the onset temperature and Tg above the 589 K test temperature, the 589 K lap shear strengths were not at the desired level of 13.79 MPa (2000 psi) desired by NASA (Samples 66, 67, and 68, Table XI).

(7) None of the lap shear samples listed in Table XI that have been air post cured at any temperature have R.T. bond strength at the 20.69 MPa (3000 psi) level desired by NASA.

The decrease in the R.T. lap shear strength on post curing in air may be at least partially accounted for by the up to 25% swelling of the adhesive bond line during the high temperature exposure. This swelling, which is caused presumably by the expansion of volatiles, increases the bond line void content, thereby reducing the bond strength. Post curing using a gradually increasing temperature from below the Tg of the bond line adhesive to 644 K (700°F) should minimize the swelling and result in higher lap shear strength levels.

4.4 EXPERIMENTS AT HIGH TEMPERATURES

The decrease in R.T. lap shear strength and the less than desired 589 K bond strength of samples post cured in stages at 589 K, 616 K, and 644 K is believed caused by the rapid evolution of the remaining volatiles from the adhesive bond line causing voids and, therefore, a porous weak bond.

In order to demonstrate that swelling is the major cause of the low lap shear strengths, the following experiments were carried out:

(1) Post curing lap shear samples free standing in air to 644 K (700°F) using a linear slow rate of temperature rise.

(2) Post curing in air while the lap shear bonds are under pressure, thereby mechanically preventing bond line swelling.

(3) Bonding at a temperature of 616 K (650°F) instead of 589 K (600°F), thereby possibly eliminating the necessity of an air post cure.

(4) Bonding at a much higher temperature (700 K, 800°F) and pressure (6.895 MPa, 1000 psi) for a short time to also produce a well-cured bond line which also does not require post cure.

The bonding conditions for the first three experiments were similar to that described in Section 3.1 with the following exceptions:

(a) Pressure was not applied until a temperature of 473 K (392°F) was reached.

(b) A bonding temperature of 616 K (650°F) was used in experiment 3.

(c) The vacuum bag post cure usually carried out immediately after bonding was eliminated. The samples were cooled while still under full vacuum and 1.38 MPa (200 psi). This bonding cycle change was used to eliminate the possibility that removal of pressure while at the bonding temperature could contribute to the swelling of the adhesive bond line.

Bondings at 700 K (800°F) were carried out using a preheated press with no vacuum bag. The holder containing the titanium coupon/adhesive lap shear assembly was inserted in the preheated press and a pressure of 6.895 MPa (1000 psi) applied immediately. The samples were, therefore, under pressure as the samples heated up. After bonding, the samples were cooled under 1.38 MPa (200 psi).

TABLE XII.

LAP SHEAR STRENGTHS OF 6/4 TITANIUM BONDED WITH EXPERIMENTAL NR-150 ADHESIVE
ADHESIVE COMPOSITION: 1:1 6FTA*:DIAMINE; 60/40 PPD*/ODA*; 65% ALUMINUM POWDER IN NMP

1	2	3	4	5	6	7	8	9	10	11	12	13
	Prepreg Volatiles Content %	Thick mm (Mils)	Bonding(1) Time Ks (Hours)	Bonding(1) Temp. K (°F)	Resin Squeeze Out	Air Post Cure Time Hours	Air Post Cure Temp. K (°F)	Lap Shear Strength(4) R.T. MPa (psi)	Lap Shear Strength(4) 589K(600°F) MPa (psi)	Failure Mode	Resin at Bond Line Onset Temp. K(°F)	Tg K(°F)
Sample #												
74	9.5	.330 (13.0)	1.8 (1/2)	589 (600)	Slight	None	—	17.33(2514) (1)		Adhesive	458 (365)	483 (410)
75	10.2	.356 (14.0)	1.8 (1/2)	589 (600)	Good	24	468 646 (383 704)	11.62(1686) (3)	1.43(208) (2)	Cohesive	583 (590)	589 (600)
76	10.2	.356 (14.0)	1.8 (1/2)	589 (600)	Good	24 "	" (Free Standing)		9.65(1400) (4)	Cohesive		
77	10.2	.356 (14.0)	1.8 (1/2)	589 (600)	Good	24	438 645 (329 702)	10.91(1583) (1)	12.89(1870) (2)	Adhesive Cohesive	583 (590)	593 (608)
78	9.2	.30 (12.0)	1.8 (1/2)	616 (650)	Slight	None (.45MPa(65 psi) pressure)	—	12.39(1797) (3)		Adhesive	523 (482)	556 (542)
79	9.2	.30 (12.0)	1.8 (1/2)	616 (650)	Slight	None	—		.81(117) (4)	Cohesive		
80	3.6	.30 (12.0)	0.3 (5 min.)	700 (800)	Slight	None	—	19.46(2822) (1)	4.43(642) (2)	Adhesive Cohesive	523 (482)	583 (590)
81(3)	3.0	.356 (14.0)	0.6 (10 min.)	700 (800)	Good	None	—	19.56(2837) (2)	7.12(1033) (3)	Adhesive Cohesive		

*6FTA: 2,2 bis(3',4'-dicarboxyphenyl) hexafluoropropane
PPD: paraphenylenediamine; ODA: oxydianiline

(1) Bonding pressure: 1.38 MPa (200 psi)
(2) Bonding pressure for Samples 80 and 81: 6.895 MPa (1000 psi)
(3) Sample 81 vented 0.6 Ks (10 min.) at 700 K (800°F) no pressure before cooling under 1.38 MPa (200 psi)
(4) Number in parenthesis under the lap shear strength indicates number of samples tested

The results of these bonding studies are given in Table XII, which includes a non-post cured control sample (Sample 74). Although four lap shear samples have been bonded simultaneously, in some cases one sample was used for TMA analysis, two of the samples were tested at one temperature, and a single sample at the other.

The results of this study are summarized as follows:

(1) Air post curing using a slow temperature increase to 646 K (704°F) over 24 hours increases the 589 K lap shear strength but decreases the R.T. strength (compare Samples 75 and 76 with Sample 74, Table XII).

(2) The bond strengths of samples post cured using a slow rate of temperature rise are no better than these obtained using a constant temperature post cure at three increasing temperatures (compare Samples 75 and 76, Table XII with Samples 66 and 67, Table XI). The similarity in bond strengths obtained from these two methods of post curing is not surprising as both methods caused about a 25% swelling of the adhesive bond line.

(3) Bonding at 616 K (650°F) instead of at 589 K (600°F), surprisingly, shows no improvement in the bond strengths at either R.T. or 589 K (compare Samples 78 and 79 with Sample 74, Table XII).

(4) Post curing in air while applying a positive pressure of 0.45 MPa (65 psi) to the bond line produces a further improvement in 589 K lap shear strength. This post cure, which was carried out using a press with a slow rate of temperature rise, produced samples which had no measurable bond line swelling and resulted 589 K lap shear strengths of 12.89 MPa (1870 psi). This bond strength is significantly higher than the bond strength of 9.65 MPa (1400 psi) obtained using a similar post cure procedure without pressure (compare Samples 77 and 76, Table XII).

(5)   Surprisingly, post curing lap shear sample under pressure to prevent bond line swelling gave no improvement in the R.T. lap shear strength (compare Samples 77 and 75, Table XII). Although the R.T. bond strengths of the samples post cured with and without pressure were similar, the mechanism of failure was different. The sample post cured free standing failed cohesively within the bond line, whereas the sample post cured under pressure failed adhesively at the adhesive/metal interface.

(6)   Bonding with no vacuum bag at 6.895 MPa (1000 psi) and 700 K (800°F) for short times gave improved R.T. bond strengths but still inferior 589 K strengths (Samples 80 and 81, Table XII). It would have been expected that bonding at a temperature of 700 K (800°F) for at least 0.9 Ks (15 mins.) would result in a completely cured adhesive bond line and, therefore, high 589 K bond strengths. However, Sample 81, Table XII, which had good resin flow in the bond line had a 589 K lap shear strength of only 7.12 MPa (1033 psi) and failed cohesively within the bond line.

(7)   TMA measurements on a titanium/adhesive/titanium sandwich cut from an untested lap shear specimen indicate that none of the bonding and post cure processes used in Table XII produced adhesive bond lines with both the onset temperature and Tg of the resin above 589 K. Although air post curing does markedly change the shape of the TMA curve (compare Figure 11 with Figure 12 and 13), the bond lines are still not competely cured.

4.5   FINAL POST CURE EXPERIMENTS

The data in Section 4.4 indicated that a 86.4 Ks (24 hour) post cure with a linear increase in temperature resulted in an undesired degree of adhesive bond line swelling (~25%) and less than desired lap shear strengths using titanium adherends. The use of a longer air post cure time with a more gradual temperature increase to improve the lap shear strengths was investigated. This investigation was carried out using two different NR-150 adhesive solutions: adhesive solution Composition D (Section 4.2)

FIGURE 11
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 74 TABLE XII
NO POST CURE

Tg = 483 K
(410°F)

O.T. = 458 K
(365°F)

PROBE DISPLACEMENT

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450
T,°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)
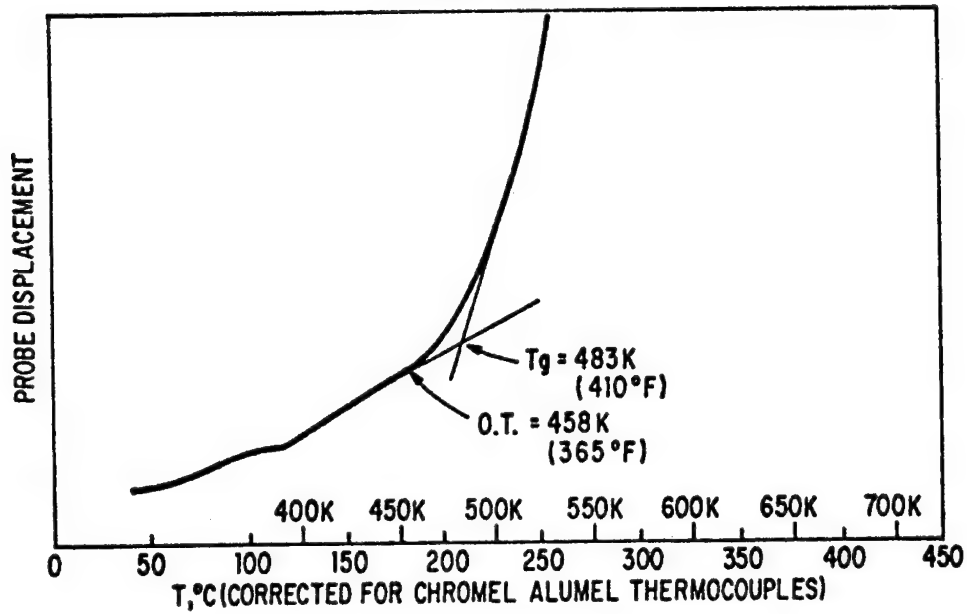
FIGURE 12
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 75 TABLE XII

AIR POST CURED 468K TO 646K
(383°F)   (704°F)

Tg = 589 K
(600°F)

O.T. = 583 K
(590°F)

PROBE DISPLACEMENT

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450
T,°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

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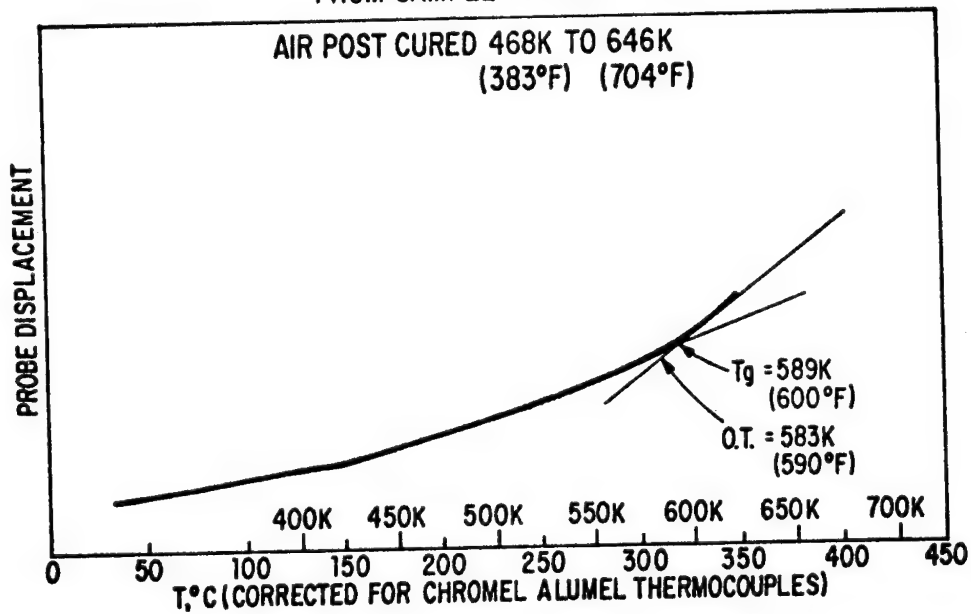
FIGURE 13
TMA CURVE OF
ADHESIVE BOND LINE
FROM SAMPLE 77 TABLE XII

AIR POST CURED WITH PRESSURE
468K TO 645K
(329°F) (702°F)

PROBE DISPLACEMENT

Tg = 593K
(608°F)
O.T.=583K
(590°F)

400K   450K   500K   550K   600K   650K   700K

0   50   100   150   200   250   300   350   400   450
T,°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)
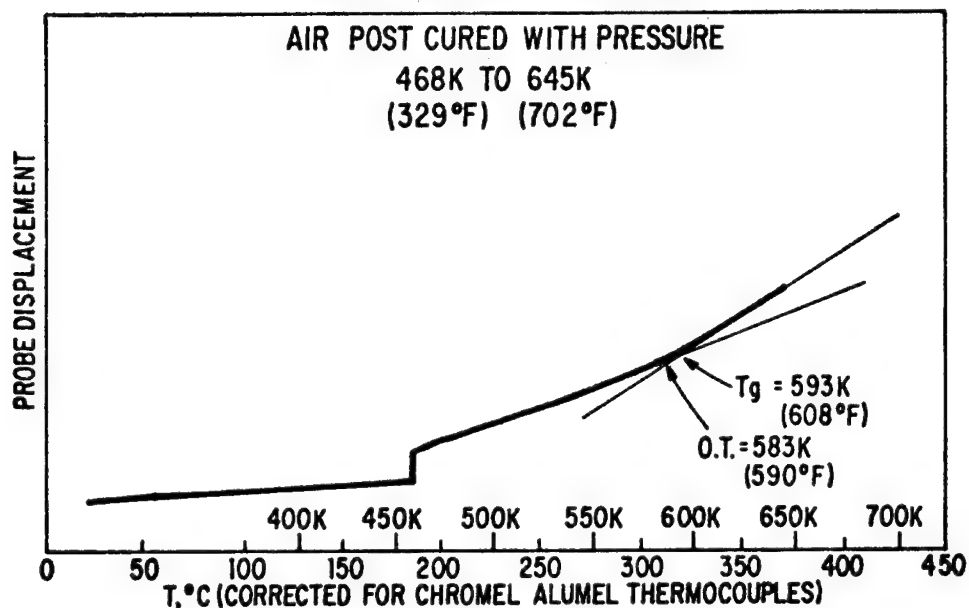
containing 65 wt. % aluminum powder, and the commercially available
NR-150B2G adhesive solution (a 95/5 mole ratio of PPD/MPD)
containing 60% aluminum powder. This latter composition produces
well-cured neat resin with a T_g of 633 K (680°F) which is 16 K
above the well-cured resin T_g of 617 K (652°F) for polymer from
solution Composition D. Use of this higher resin T_g system should
result in post cured adhesive bond lines with resin T_g's well above
589 K and, therefore, higher 589 K bond strengths.

Two different autoclave-type bonding cycles were employed
using a vacuum bag in a press: one in which a single bonding
temperature of 589 K (600°F) at 1.38 MPa (200 psi) was employed
and one in which a lower temperature of 433 K (320°F) was used at
1.38 MPa (200 psi), followed by a temperature of 589 K (600°F) at
a lower pressure of 0.52 MPa (75 psi). This latter procedure has
been found to successfully reduce the volatile content of a
graphite fiber/NR-150B2 molding to a level which produces a
blister-free laminate on a subsequent free standing post cure.

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TABLE XIII.

EFFECT OF ADHESIVE COMPOSITION, BONDING AND POST CURE CONDITIONS
ON BOND STRENGTHS OF NR-150 BONDED TITANIUM LAP SHEAR SAMPLES

1	2	Bonding Conditions			Post Cure Conditions			9	Lap Shear Strength		12	13
	Prepreg Volatile Content	3	4	5	6	7	8	Increase in Bond Line Thickness	10	11	Bond Line Onset Temp.	Tg
Sample #	%	Time Ks (Hours)	Temp. K(°F)	Pressure MPa.psi	Atmosphere	Time Ks (Hours)	Temperature K(°F)	%	R.T. MPa.(psi)	589 K(600°F) MPa.(psi)	K(°F)	K(°F)
Adhesive Composition: 1:1 6FTA*:diamine 60/40 PPD*/ODA* 65% Aluminum Powder in NMP*												
82	9.2	3.6 (1)	589(600)	1.38(200)	Vacuum Bag; Air	3.6 (1); 14.04(39)	589(600); 431→662 (316→732)	16.2	10.80(1566)	8.78(1273)		
83	9.2	3.6 (1)	589(600)	1.38(200)	Air	14.04(39)	431→662 (316→732)	18.8	10.47(1518)	10.50(1523)	603 (626)	612 (642)
84	9.2	5.4 (1 1/2)	589(600)	1.38(200)	Air	14.04(39)	431→662 (316→732)	19.6	10.20(1479)	9.72(1410)	None	>725 (658)
85	9.5	1.8 (1/2); 7.2 (2)	433(320); 589(600)	1.38(200); 0.52(75)	None	—	—	—	17.84(2587)			
86	9.5	1.8 (1/2)	433(320); 589(600)	1.38(200); 0.52(75)	Air	144. (40)	426→662 (308→732)	9.1	12.05(1749)	8.94(1297)		
87	9.5	1.8 (1/2); 3.6 (1)	433(320); 589(600)	1.38(200); 0.52(75)	Air	144. (40)	426→662 (708→732)	16.2	9.42(1366)	9.34(1354)		
NR-150B2G Adhesive: 1:1 6FTA*:diamine 95/5 PPD*/MPD* 60% Aluminum Powder in NMP*												
88	11.5	3.6 (1)	589(600)	1.38(200)	None	—	—	—	13.72(1990)	2.52(366)	538 (509)	568 (563)
89	11.0	3.6 (1)	589(600)	1.38(200)	Air	136.8(38)	423→661 (306→730)	12.2	13.31(1931)	7.12(1033)	None	>668 (734)
90	10.5	1.8 (1/2); 5.4 (1 1/2)	589(600); 589(600)	1.38(200); 0.52(75)	Air	75.6(21)	589(600)	9.6	13.27(1925)	9.49(1377)		
91	10.5	1.8 (1/2); 3.6 (1)	433(320); 589(600)	1.38(200); 0.52(75)	Air	Not Post Cured —; 144. (40)	Not Post Cured —; 424→662 (304→732)	10.7	10.95(1588); 4.56(662)	7.34(1064)		
92	10.5	1.8 (1/2); 7.2 (2)	433(320); 589(600)	1.38(200); 0.52(75)	Air	Not Post Cured —; 144. (40)	Not Post Cured —; 424→662 (304→732)	17.9	15.62(2267); 5.19(752)	4.61(668)		

*6FTA: 2,2 bis(3',4'-dicarboxyphenyl) hexafluoropropane;
PPD: paraphenylenediamine; ODA: oxydianiline; MPD: metaphenylenediamine; NMP = N-methylpyrrolidone

From the results of these investigations which are summarized in Table XIII, it can be concluded that

(1) A free standing air post cure using a very slow rate of temperature rise of .0016 K/s (~0.2°F/min.) appears no better than the post cure conditions previously used in producing high lap shear bond strength levels at both R.T. and 589 K.

(2) There appears no difference in the lap shear bonds produced using either of the two adhesive compositions or bonding cycles.

(3) In all cases, post curing reduces the R.T. lap shear strengths and increases the 589 K strength to a maximum of 10.34 MPa (1500 psi).

(4) The bond levels desired by NASA - 20.69 MPa (3000 psi) at R.T. and 13.79 MPa (2000 psi) at 589 K - were not attained with any of the conditions used.

4.6 BONDING AT HIGH TEMPERATURES AND PRESSURES

It was increasingly apparent that the high bond strength levels desired at both R.T. and 589 K (600°F) are not easily attained with titanium adherends using the temperature and pressure limitation imposed by NASA and the adhesive systems developed to date. The use of higher temperatures and pressures similar to the conditions used for Samples 80 and 81, Table XII was, therefore, investigated further, in order to demonstrate the ultimate capability of NR-150 adhesives. Lap shear bonds using titanium adherends, with adhesive prepreg having significantly lower volatile levels, were prepared using temperatures up to 710 K (818°F) and pressures up to 20.68 MPa (3000 psi) in a press without a vacuum bag.

As with the vacuum bag autoclave conditions, four bonds were made at once using four finger 50 mil 6/4 titanium coupons using a holder to align the metal adherends and contain a thermocouple. The titanium surfaces were etched and primed using the procedures in Appendix A and B, Part I. The holder containing the titanium/ adhesive prepreg/titanium assembly was put in a preheated press

TABLE XIV.

HIGH TEMPERATURE BONDING WITH
EXPERIMENTAL NR-150 ADHESIVE AND TITANIUM ADHERENDS

Sample #	Bonding Conditions Temperature K(°F)	Time Seconds	Time Mins.	Pressure MPa (psi)	Lap Shear Strength @ R.T. MPa (psi)	@589 K(600°F) MPa (psi)	Remarks
93	R.T.→661(730)→680(764)→698(797)→706(812) Cool	180 / 60 / 240 / 300	3 / 1 / 4 / 5	None / 6.89(1000) / None(Venting) / 6.89(1000) / 1.38(200)	15.07 (2186)	6.30 (9.14)	Incomplete Bond
94	423(302)→655(720)→695(792)→700(800) Cool	300 / 600 / 300	5 / 10 / 5	6.89(1000) / None(Venting) / 6.89(1000) / 1.38(200)	18.15 (2633)	4.65 (674)	Incomplete Bond
95	473(392)→653(716)→684(772)→701(802)→706(812) Cool	300 / 180 / 300 / 300	5 / 3 / 5 / 5	6.89(1000) / None(Venting) / 6.89(1000) / None(Venting) / 1.38(200)	21.60 (3133)	5.96 (865)	Cohesive Failure
96	R.T.→628(671)→653(716)→673(752)→700(800) Cool	180 / 120 / 120 / 780	3 / 2 / 2 / 13	6.89(1000) / None(Venting) / 6.89(1000) / None(Venting) / 1.38(200)	21.80 (3161)	5.55 (805)	Incomplete Bond
97	473(392)→690(797)→707(814) Cool	600 / 600	10 / 10	6.89(1000) / None(Venting) / 1.38(200)	19.56 (2837)	7.13 (1033)	Cohesive Failure
98	R.T.→690(782)→701(802) Cool	600 / 900	10 / 15	6.89(1000) / None(Venting) / 1.38(200)	17.44 (2530)	9.29 (1347)	Incomplete Bond
99	348(167)→691(784)→701(802) Cool	600 / 1020	10 / 17	6.89(1000) / None(Venting) / 1.38(200)	14.90 (2161)	9.06 (1314)	Adhesive Failure @ R.T. Cohesive Failure @ 589 K
100	448(347)→709(816)→810(818) Cool	900 / 600	15 / 10	1.38(200) / None(Venting) / 1.38(200)	14.08 (2042)	5.40 (783)	Incomplete Bond
101	R.T.→613(644)→667(742)→677(760)→700(800)→704(808) Cool	120 / 240 / 60 / 300 / 300	2 / 4 / 1 / 5 / 5	None / 13.79(2000) / None(Venting) / 20.68(3000) / None(Venting) / 1.38(200)	16.82 (2410)	5.96 (846)	Cohesive Failure Fabric Distorted

Bonds made using adhesive prepreg .33 mm (13 mils) thick ~2% volatiles

Adhesive Solution: 1:1 6FTA:diamine; 60/40 PPD/ODA
65% aluminum powder in NMP

6/4 titanium coupons etched using "Pasajell" 107 then primed with .013 mm (1/2 mil) coating of adhesive solution and "B" staged 1.8 Ks (1/2 hour) at 418 K (293°F)

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and bonded according to the schedules in Table XIV. Adhesive solution Composition D - 1:1 6FTA:diamine, 60/40 PPD/ODA, 48 wt. % cured resin solids in NMP containing 65% aluminum powder was used for preparing prepreg for this study. Prepreg with volatile levels of about 2 wt. % was prepared by "B" staging up to 478 K (401°F). The results of tests on lap shear samples prepared under various bonding conditions are given in Table XIV. Bonding pressures of 1.38 MPa (200 psi) to 20.89 MPa (3000 psi) were evaluated. Variations of time at which the pressure is first applied, pressure dwell times and venting times were all evaluated.

In general, the results of bonding at high temperatures and pressures are disappointing. As has been found with low pressure, low temperature bonding, followed by a post cure, higher 589 K (600°F) lap shear strengths usually occur with lower R.T. strengths. Bond strengths above 6.89 MPa (1000 psi) at 589 K are obtained when bonding at 700 K (800°F) only when a venting (post cure) time of at least 10 minutes is used. (See Samples 97, 98, and 99, Table XIV.) Use of lower pressures (Sample 100) or pressures over 6.89 MPa (1000 psi) (Sample 101) do not result in improved bond strengths. It appears that adhesive prepreg having ~2% volatiles has border line resin flow at the temperatures used as several of the lap shear bonds exhibited incomplete bonding.

When **time permits, further evaluation of bonding at high** temperatures and pressures should be made using the commercial NR-150B2G composition as well as Composition D (Section 4.2). The effect of bonding with and without the use of a glass cloth scrim and the effect of other titanium surface treatments should be evaluated.

4.7 WIDE AREA BONDING

The work reported above on bonding titanium lap shear samples using NR-150 adhesive solutions based on NMP indicated that this adhesive system would be unsatisfactory for preparing wide area bonds. The unsolved problem associated with the removal of the last traces of volatiles in the preparation of

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TABLE XV.

WIDE AREA BONDING OF TITANIUM
USING NMP BASED NR-150 ADHESIVE SOLUTIONS

.1524 m x .1524 m (6" x 6") 6/4 titanium panels
Bonded using adhesive Composition D containing 65 wt. % aluminum powder

Sample #	Adhesive Prepreg Thick mm (Mils)	Adhesive Prepreg % Volatiles	Adhesive(1) Bond Line Thickness mm (Mils)	Strength of Lap Shear Sample Taken From Center of Bond @ R.T. MPa (psi)	@ 589 K MPa (psi)	Failure Mode	Adhesive Bond Line Onset Temp. K (°F)	Adhesive Bond Line Tg K (°F)
A	.352 (14.0)	9.0	.762 (30.0)	14.00 (2031)		Cohesive	545 (523)	545 (523)
B	.356 (14.0)	9.0	.673 (26.5)	11.25 (1632)		Cohesive	533 (500)	549 (528)
C	.165 (6.5)	6.4	.280 (11.0)	9.23 (1338)		Cohesive	548 (587)	551 (532)
D	.300 (12.0)	8.0	.749 (29.5)	13.75 (1994)		Cohesive	548 (527)	573 (572)

The following sample was post cured in air 86.4 Ks (24 hours) 473 K (392°F)

Sample #	Adhesive Prepreg Thick mm (Mils)	Adhesive Prepreg % Volatiles	Adhesive(1) Bond Line Thickness mm (Mils)	Strength of Lap Shear @ R.T. MPa (psi)	@ 589 K MPa (psi)	Failure Mode	Adhesive Bond Line Onset Temp. K (°F)	Adhesive Bond Line Tg K (°F)
E	.300 (12.0)	8.0	.597 (23.5) After Post Cure .648 (25.5)	646 K (685°F)(2) 6.46 (937)	6.50 (942)	Cohesive	568 (563)	583 (590)

(1) Measured in center of sandwich panel
(2) Measured on sample about 50.5 mm (2") from edge
(3) Measured after post cure

Bonding Conditions: Heat under full vacuum at 2.2 K (4°F)/min. R.T. to 589 K (600°F)
Apply 1.4 MPa (200 psi) at 473 K (392°F)
Hold 1/2 hour at 589 K, full vacuum, 1.4 MPa (200 psi)
Post cure 1 hour at 589 K, full vacuum only
Cool to R.T. under full vacuum

standard 12.7 mm (1/2 inch) x 25.4 mm (1 inch) lap shear bonds would be even more difficult to solve on preparing titanium bonded sandwich panels up to .254 m x .254 m (10 inches x 10 inches). As the contract with NASA required the delivery of two wide area bonded panels using titanium adherends, the bonding of wide areas was evaluated.

4.7.1 Bonding Using a Press

Five wide area (.1524 m x .1524 m; 6" x 6") 6/4 titanium panels were bonded under simulated autoclave conditions using a vacuum bag in a press. The titanium surfaces were etched and primed using the procedure in Appendix A and Appendix B, Part II. The adhesive prepreg was prepared using the procedure in Appendix D using the adhesive solution Composition D (Section 4.2) containing 65 wt. % aluminum powder filler. One wide area bond was made using a thinner adhesive prepreg prepared using a single coating process similar to that described in Section 3.1. All five wide area bonds were made using the procedure at the bottom of Table XV.

Conclusions based on the bonding of .1524 m x .1524 m (6" x 6") titanium panels using a vacuum bag in a press as summarized in Table XV are as follows:

(1) In all cases, the bond strengths (at room temperature) of lap shear samples cut from the center of the bonded panel are low. For example, bond strengths of 9.23 MPa (1338 psi) to 14.00 MPa (2031 psi) were obtained vs over 20.69 MPa (3000 psi) for conventional lap shear samples using the same adhesive system.

(2) The failure mode of all samples from the wide area bonds is cohesive within the adhesive layer. This is to be contrasted with failure between the metal substrate and the adhesive layer for conventional lap shear samples.

(3) The bond lines produced in the center of the wide area bonds are abnormally thick (~.762 mm, 30 mils) using prepreg .305-.356 mm (12-14 mils) thick which produces .127-.203 mm

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(5-8 mils) bond lines in conventional lap shear samples.

These results can only be explained by the entrapment of volatiles in the center of the wide area bond producing a swollen porous weak bond.

(4) Use of a thinner lower volatile prepreg (Sample C, Table XV), although producing a thinner bond line, does not give improved bond strengths in the center of a wide area bond.

(5) Post curing a wide area bonded panel in air (Sample E, Table XV) does not improve the R.T. bond strength and, in fact, lowers the strength. The post cure also does not produce 589 K bond strengths equal to that resulting from post curing conventional lap shear samples.

(6) TMA analysis of the center section of the wide area bonds indicates that the Tg of the adhesive resin in the bond line (545 K to 572 K) is well below the 589 K temperature desired. Even after a post cure up to 646 K (685°F), the Tg of the adhesive in the center of the bond line is still below the desired level.

4.7.2 Autoclave Bonding

The work bonding .1524 m x .1524 m (6" x 6") titanium panels indicated that acceptable bond strengths can probably be obtained if at all only using long bonding cycles at temperatures well above 589 K. As time constraints in the NASA contract prevented further investigation using the press, wide area .254 m x .254 m (10" x 10") bonded titanium panels were then prepared in a autoclave.

Two .254 m x .254 m (10" x 10") titanium bonded panels were prepared using a small autoclave at Rockwell International, Space Division, Downey, California. The titanium panels were etched and primed as indicated in Appendix A and Appendix B, Part II. Both panels were bonded using the following bonding conditions:

(a) Heat from R.T. to 461 K (370°F) at .033 K/second (5°F/min.) under full vacuum.

(b) Apply 1.38 MPa (200 psi) over 54 Ks (15 mins.) from 461 K (320°F) to 480 K (405°F).

(c) Heat to 589 K (600°F) at .033 K/second (5°F/min.) full vacuum, 1.38 MPa (200 psi).

(d) Bond 3.6 Ks (1 hour) at 589 K full vacuum and 1.38 MPa (200 psi).

(e) Cool to 339 K (150°F) under full vacuum and 1.38 MPa (200 psi).

One panel was bonded using prepreg based on adhesive solution Composition D (Section 4.2) containing 65 wt. % aluminum powder filler prepared using the procedure in Appendix D which produced prepreg .279 mm (11 mils) thick with a 9.3% volatile content. A lap shear sample cut out of the center of the panel had a 7.66 MPa (1109 psi) R.T. bond strength exhibiting cohesive failure and a bond line adhesive resin Tg of 517 K (468°F).

The R.T. bond strength and resin Tg from the center of this .254 m x .254 m (10" x 10") panel are lower than those obtained from the .1524 m x .1524 m (6" x 6") panels probably because of the greater distance required for the volatiles to diffuse from the center of the panel.

A second .254 m x .254 m (10" x 10") autoclave bonded panel was bonded with thinner (.203 m, 8 mils) lower volatile (5.5%) adhesive prepreg based on the same adhesive solution as in the first panel.

Although the same bonding conditions were used as the first panel, the adhesive bond was of such poor quality that the bonds delaminated on cutting a lap shear sample from the center of the bonded area. Failure occurred between the primed surface and the adhesive prepreg indicating insufficient adhesive resin flow.

4.7.3 Conclusions

It is unlikely that wide area bonds using titanium adherends and adhesives based on NR-150 solutions containing NMP

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can be produced with acceptable bond strengths. The prepreg
volatile levels required to give good resin flow and, therefore,
good bonding result in high void, weak bonds. The distance from
the center of the panel to the edge is too long for the volatiles
to diffuse out in a reasonable time at the temperature used for
bonding.

Two bonded panels .254 m x .254 m (10" x 10") wide were
prepared in the autoclave using 6/4 titanium adherends and adhe-
sive prepreg based on NR-150 adhesive solution Composition D
containing 65 wt. % aluminum powder filler for delivery to NASA.

5.   ADHESIVE SOLUTIONS BASED ON DIGLYME

From the work reported in Section 4, it can be concluded that it is extremely difficult to obtain acceptable R.T. and 589 K (600°F) lap shear bonds using titanium adherends and NR-150 adhesive solutions based on NMP solvent. As the presence of even small (<0.25%) amounts of NMP in NR-150 resins significantly reduces the polymer Tg, the difficulty in removing the last traces of NMP may be the cause of the problem. The best combination of lap shear strengths obtained with NR-150 adhesive solutions based on NMP are 11.72 MPa (1700 psi) at R.T. and 9.65 MPa (1400 psi) at 589 K (600°F). These strength levels are well below the 20.69 MPa (3000 psi) at R.T. and 13.79 MPa (2000 psi) levels desired by NASA. Higher levels have been obtained at R.T. but with much lower levels at 589 K and higher levels have been obtained at 589 K, but only using an impractical post cure with the bond line under pressure.

One way of avoiding the problems associated with NMP is to replace it with another solvent. One solvent suggested by NASA personnel as a good candidate to replace NMP is diglyme. A quick experiment indicated that the monomers used in NR-150 adhesive solutions were soluble in diglyme. Adhesive prepreg was, therefore, prepared from solutions based on diglyme and evaluated in lap shear samples. A report of this work follows.

5.1   PRELIMINARY EVALUATION

Adhesive solutions using three different NR-150 compositions were prepared using diglyme as the solvent as indicated in Table XVI.

TABLE XVI

CANDIDATE ADHESIVE COMPOSITIONS
BASED ON DIGLYME SOLVENT

Solution Designation	Solution Composition 48 Wt. % in Diglyme	Tg of Molding
E	1:1 6FTA:diamine 60/40 PPD/ODA	605 K (630°F)
F	1:1 6FTA:diamine 75/25 PPD/ODA	617 K (652°F)
G	1:1 6FTA:diamine 95/5 PPD/MPD	633 K (680°F)

In the initial experiments, titanium lap shear coupons were bonded using prepreg based on Solution E, Table XVI, containing 65 wt. % aluminum powder. For this evaluation, the titanium surface was etched using the procedure in Appendix A and primed within 1.8 Ks (1/2 hour) after etching using a procedure similar to that in Appendix E, Steps 2-5. The adhesive prepreg was prepared using the procedure in Appendix F. The lower boiling point of diglyme (435 K, 324°F) as compared to NMP (477 K, 400°F) requires some process changes.

For example, this difference requires the use of lower temperatures during the initial stages of "B" staging to prevent foaming of the resin caused by the more rapid evolution of the solvent.

The results of tests on the initial lap shear bonds made using diglyme solution are given in Table XVII. Although the adhesive prepreg has not been optimized as indicated by the thicker than desired bond lines, it is apparent that a significant improvement in the bond strengths at both R.T. and 589 K has been achieved over the best obtained using NMP solutions.

Although R.T. lap shear strengths above 20.69 MPa (3000 psi) have readily been achieved using NMP solutions and 589 K (600°F) lap shear strengths of over 10.34 MPa (1500 psi) have been obtained previously, this is the first instance during the work

TABLE XVII.

LAP SHEAR STRENGTHS OF TITANIUM
BONDED WITH NR-150 ADHESIVE BASED ON DIGLYME SOLUTION

Sample	Post Cure Conditions	Bond Line Thickness mm (Mils)	Lap Shear Strengths @ R.T. MPa (psi)	@ 589 K MPa (psi)	Failure Mode
102	None	.292 (11.5)	24.14 (3509)	Not Tested	Cohesive
103	None	.292 (11.5)	22.02 (3204)	12.09 (1753)	Cohesive
104	140.4 Ks 39 Hour in Air Free Standing 427K→662K (309°F)→(732°F)	.305 (12.0)	16.89 (2540)	12.29 (1855)	Cohesive

(1) Bonding Conditions: R.T. 589K(600°F) at .033 K/sec. (5°F/min.) under full vacuum, 1.38 MPa (200 psi) then 1.8 Ks (1/2 hour) bonding, full vacuum, 1.38 MPa (200 psi) at 589 K (600°F) and 3.6 Ks (1 hour) post cure, full vacuum, zero pressure at 589 K (600°F)

(2) Prepreg: .33 mm (13 mils) thick; 8-9% volatiles; scrim cloth: 112-38 Style E glass I-621 finish

on this contract that such high bond strengths have been obtained simultaneously at both temperatures, e.g., 22.02 MPa (3204 psi) at R.T. and 12.09 MPa (1753 psi) at 589 K. It is all the more significant that these high values have been obtained at 589 K without a post cure.

Post curing up to 662 K (732°F) samples bonded using prepreg based on diglyme solutions causes a slight increase in 589 K lap shear strength and a decrease in the R.T. lap shear strength (Sample 104, Table XVII). Although this effect of post curing is similar to that found with samples bonded with prepreg from NMP solutions, the 4 1/2% swelling of the bond line is significantly lower with diglyme solutions.

The results indicate that, as previously stated, the major factor preventing the attainment of high 589 K lap shear strengths using adhesives based on NMP solutions has been the difficulty in removing the last traces of NMP from the bond line. By replacing NMP with diglyme having a lower boiling temperature, being a less polar and a more linear molecule, the diffusion through and volatilization of the solvent out of the adhesive resin is more readily accomplished.

5.2 EFFECT OF ADHESIVE COMPOSITION

The next experiments using titanium adherends were made to confirm the initial results and to investigate bonding using the other two compositions listed in Table XVI. The results of these experiments are given in Table XVIII, which is divided into three sections. In the top section of the table, lap shear strengths of bonds made using prepreg having various volatile contents using Composition E, Table XVI, are given, and lap shear strengths of bonds from prepreg based on solution Compositions F and G, Table XVI, are given in the following sections. None of the lap shear samples have been post cured. In most cases, the lap shear strengths reported are an average of two samples, with both values indicated underneath the average.

TABLE XVIII.

LAP SHEAR STRENGTHS OF TITANIUM BONDED WITH EXPERIMENTAL NR-150 ADHESIVES BASED ON DIGLYME

| | Adhesive Composition | | | Adhesive Prepreg | | Resin at Bond Line | | Lap Shear Strength | | |
| | | | Aluminum | Thick | | | Thick | @ R.T. | @589 K (600°F) | |
Sample	Diamines	Mole Ratio	Powder %	mm (Mils)	Volatiles %	Flow	mm (Mils)	MPa (psi) (Range in psi)	MPa (psi) (Range in psi)	Failure Mode
105	PPD/ODA*	60/40	65.	.38 (15)	8.1	Slight	.267 (10 1/2)	24.96 (3620)	4.10 (545) (479-711)	50% adhesive at R.T. adhesive at 589 K
106	"	"	"	.254 (10)	10.0	Good	.127 (5)	20.26 (2939) (2773-3104)	6.54 (949) (267-1631)	Adhesive at R.T. Adhesive to cohesive at 589 K
107	"	"	"	.38 (15)	11.8	Excessive	.114 (4 1/2)	20.08 (2912) (2799-3025)	11.55 (1675) (1373-1976)	Adhesive at R.T. More or less cohesive at 589 K
108	"	"	"	.38 (15)	9.2	Slight Good	.24 (9 1/2)	23.09 (3349) (3150-3548)	7.69 (1116) (1105-1127)	80% cohesive at R.T. 50% cohesive at 589 K
109	PPD/ODA	75/25	65.	.23 (9)	10.5	Slight Good	.089 (3 1/2)	17.45 (2531) (2457-2605)	11.72 (1700) (1327-2071)	Adhesive at R.T. 20% cohesive at 589 K
110	"	"	"	.38 (15)	12.5	Excessive	.102 (4)	17.44 (2529) (2516-2542)	14.12 (2048) (2016-2080)	Adhesive at R.T. 80% cohesive at 589 K
111	PPD/MPD*	95/5	60.	.29 (11 1/2)	11.9	Good	.140 (5 1/2)	10.73 (1556)	8.01 (1170)	50% cohesive at R.T. 30% cohesive at 589 K
112	"	"	"	.38 (15)	12.2	Excessive	.114 (4 1/2)	10.14 (1471) (1372-1569)	6.58 (995) (865-1042)	Adhesive at R.T. 80% adhesive at 589 K

Bonding conditions using a press: 2 K/min.; R.T. to 589 K (600°F) under full vacuum and 1.38 MPa (200 psi); then 1 hour at 589 K, 1 hour at 589 K, full vacuum, 1.38 MPa (200 psi); then 1 hour at 589 K, full vacuum only.

*PPD: paraphenylenediamine
ODA: oxydianiline
MPD: metaphenylenediamine

A summary of the results presented in this table is as follows:

(a)   The initial lap shear strengths reported in Table XVII are confirmed by the data in this table. Using the adhesive composition containing a 60/40 mole ratio of PPD/ODA (adhesive Composition E, Table XVI), lap shear strengths of close to 20.69 MPa (3000 psi) at R.T. and almost 11.72 MPa (1700 psi) at 589 K are obtained (Sample 107, Table 18).

(b)   Using an adhesive composition containing a 75/25 mole ratio of PPD/ODA (adhesive Composition F, Table XVI), which gives a higher well-cured resin Tg as compared to Composition E (see Figure 1), 589 K lap shear strengths of 13.79 MPa (2000 psi) are obtained (Samples 109 and 110, Table XVIII).

(c)   The R.T. lap shear strength levels of bonds produced with adhesive Composition F (17.24 MPa, 2500 psi) are below that obtained with adhesive Composition E and, therefore, below the 20.69 MPa (3000 psi) level desired by NASA (Samples 109 and 110, Table XVIII).

(d)   Bonding with prepreg from adhesive solution Composition G (Table XVI), the diglyme counterpart of the commercial NR-150B2G adhesive solution, does not produce as high bond strength levels as the other compositions at either R.T. or 589 K (Samples 111 and 112, Table XVIII).

Better control of the bond line thickness and use of an air post cure should produce improved lap shear strength levels at both R.T. and 589 K.

5.3   EFFECT OF POST CURING

As the bond strengths of titanium lap shear samples bonded with adhesive prepreg made from NR-150 adhesive solutions based on diglyme solvent were so close to the goal levels at both temperatures, a simple isothermal post cure was investigated as a way to upgrade the bond strengths to the goal levels. Etched and primed titanium coupons were bonded using two different adhesive compositions then post cured free standing overnight in 589 K (600°F) air.

The results of this evaluation using adhesive prepreg based on solution Compositions E and F, Table XVI, is given in Table XIX and summarized as follows:

(a) The R.T. and 589 K lap shear bond strength goal levels desired by NASA are met on post curing at 589 K lap shear samples bonded using adhesive solution Composition F (Samples 117 and 118, Table XIX). R.T. bond strengths of 22.06 MPa (3250 psi) to 24.13 MPa (3500 psi) and 589 K bond strengths of 14.13 MPa (2050 psi) to 15.51 MPa (2250 psi) have been obtained which are above the NASA goal levels of 20.69 MPa (3000 psi) and 13.79 MPa (2000 psi).

(b) Post curing lap shear samples bonded using adhesive Composition E does not result in bond strengths at the goal levels (Samples 114 and 115, Table XIX). In fact, post curing reduces the R.T. bond strengths from a value above the NASA goal level to a value below the goal level (compare Sample 113 with Samples 114 and 115, Table XIX).

(c) Although a post cure improves the 589 K lap shear strength of bonds made using Composition E, the NASA goal level of 13.79 MPa (2000 psi) is not attained.

(d) The highest lap shear values are obtained when lap shear failure occurs cohesively within the bond line adhesive layer. The greater the contribution of failure between the substrate and the adhesive bond line the lower the bond strength.

From the above results, it is concluded that the preferred adhesive solution composition for bonding 6/4 titanium alloy is Composition F, Table XVI, a 1:.75:.25 mole ratio of 6FTA:PPD:ODA, 48 wt. % cured resin solids in diglyme, containing 65 wt. % aluminum powder (Reynolds Grade 1-131 atomized) filler (based on total cured solids). This solution is used to both prime the adherend surface and to prepare adhesive prepreg. The lap shear samples are bonded using autoclave conditions at 589 K and post cured for 57.6 Ks (16 hours) at 589 K. The specific processes used to prepare lap shear samples using titanium adherends are given in Appendices A, E, F, and G attached to this report.

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TABLE XIX

EFFECT OF POST CURING ON LAP SHEAR STRENGTHS OF TITANIUM BONDED
WITH DIGLYME BASED ADHESIVES

Sample	Adhesive Composition PPD/ODA* Ratio	Adhesive Prepreg Thick mm (Mils)	Volatiles %	Resin at Bond Line Flow	Thick mm Mils	Post Cure in Air Time Hours	Temp. K (°F)	Lap Shear Strength @ R.T. MPa (psi) (Range in psi)	@ 589 K (600°F) MPa (psi) (Range in psi)	Failure Mode
113	60/40 (Comp. E)	.38 (15)	9.3	Good	.17-.20 (6.5-8.0)	None		21.59 (3131) (3023-3238)	5.44 (789) (785- 793)	50% adhesive at R.T. and 589 K
114	"	.41 (16)	9.6	Excessive	.14-.19 (5.5-7.5)	16	589 (600)	18.53 (2687) (2504-2859)	8.54 (1238) (966-1510)	75% adhesive at R.T. and 589 K
115	"	.23 (9)	9.9	Slight to Good	.10-.13 (4.0-5.0)	16	589 (600)	17.28 (2502) (2098-2906)	11.05 (1602) (1558-1646)	80% adhesive at R.T. 60% cohesive at 589 K
116	75/25 (Comp. F)	.38 (15)	12.6	Excessive	.08-.10 (3.0-4.0)	None		17.78 (2578) (2530-2626)	10.11 (1460) (1203-1729)	100% adhesive at R.T. 75% adhesive at 589 K
117	"	.38 (15)	12.7	Excessive	.11 (4.5)	16	589 (600)	24.18 (3507) (3303-3712)	15.55 (2255) (2208-2301)	100% cohesive at R.T. and 589 K
118	"	.20 (8)	10.6	Good	.11-.13 (4.5-5.0)	16	589 (600)	22.39 (3248) (3225-3272)	14.23 (2064) (2001-2128)	90% cohesive at R.T. and 589 K

Adhesive Composition: 1:1 6FTA*:diamine; PPD/ODA ratio as indicated; 48% cured resin in diglyme;
65% aluminum powder based on total cured solids.

Bonding Conditions: 2K/minute under full vacuum, 1.38 MPa (200 psi); Bond one hour at 589 K (600°F)
full vacuum, 1.38 MPa (200 psi); Hold one hour at 589 K (200 psi) full vacuum only;
Cool under full vacuum only.

*6FTA: 2,2 Bis(3',4'-Dicarboxyphenyl)hexafluoropropane
 PPD: Paraphenylenediamine
 ODA: Oxydianiline

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6. COMPARISON OF NMP AND DIGLYME SOLUTIONS

The replacement of the NMP (N-methylpyrrolidone) solvent with diglyme (dimethyl ether of diethylene glycol) in NR-150 adhesive solutions results in a dramatic improvement in the processibility of the adhesive as well as improvement in the lap shear strengths using titanium adherends. Comparison of the lap shear strengths obtained on bonding titanium with adhesive solutions which differ only in the solvent using similar bonding conditions is made in Table XX. Simulated autoclave conditions were used with both adhesive systems, bonding at 589 K (600°F) and 1.38 MPa (200 psi) with a vacuum bag in a press. The bonded samples were then post cured 57.6 Ks (16 hours) at 589 K (600°F).

The lap shear strengths of the samples bonded using NMP solutions (see Samples 68-69, Table XI) are lower than those bonded using diglyme solutions and are lower than the NASA goal levels - 20.69 MPa (3000 psi) at R.T. and 13.79 MPa (2000 psi) at 589 K (600°F). Higher lap shear strengths than those indicated in Table XX have been obtained using other NMP based adhesive compositions. However, with the other compositions, conditions which gave good R.T. lap shear strengths result in poor 589 K strengths, and conditions which gave good 589 K strengths result in poorer R.T. strengths. Only the lap shear samples prepared from adhesive prepreg based on diglyme solutions exceed the NASA goal level bond strengths at both R.T. and 589 K (600°F).

Optical examination of the surfaces of the failed lap shear samples also shows differences in the bonds made using adhesives based on the two solvents. The surfaces from samples tested at R.T. and 589 K (600°F) are shown in Figures 14 and 15, respectively. These samples were bonded with adhesive compositions containing a 60/40 PPD/ODA mixture using simulated autoclave conditions, bonding at 589 K (600°F) at 200 psi without an air post cure.

TABLE XX.

EFFECT OF SOLVENT USED IN ADHESIVE SOLUTION
ON BOND STRENGTHS OF TITANIUM BONDED WITH
AN EXPERIMENTAL NR-150 ADHESIVE

Solvent For Adhesive Solution	Lap Shear Strength		
	NMP	Diglyme	NASA Goal
At Room Temperature	19.23 MPa (2790 psi)	24.13 MPa (3500 psi)	20.69 MPa (3000 psi)
At 589 K (600°F)	6.07 MPa (880 psi)	15.13 MPa (2200 psi)	13.79 MPa (2000 psi)

Adhesive Composition:

  1:1 6FTA:diamine
  75/25 PPD/ODA
  48 wt. % resin in solution
  65% aluminum powder

  Samples Post Cured, 16 Hours in Air at 589 K (600°F)

The two photographs of the failed adhesive surfaces shown
in Figure 14 differ in several ways. The surface on the left from
a lap shear sample made using an NMP solution shows a relatively
smooth surface because the failure at R.T. was mainly adhesive
(between the adhesive and the titanium surface). The mating
adherend is not shown. However, in the few places where the
adhesive layer next to the metal surface has been removed, holes
or voids (dark areas) can be seen.

In contrast to the surface of the adhesive based on NMP, the
picture on the right in Figure 14 shows the surface of the adhe-
sive after testing a lap shear sample prepared using diglyme based
solutions. In this case, the failure is cohesive (within the resin
next to the glass scrim carrier surface). The mating surface (not
shown) is covered with adhesive resin only. In this picture,
holes are visible (dark areas) in only a few places between the
cross-over points of the glass fabric scrim.

FIGURE 14

PHOTOMICROGRAPHS OF THE FAILED ADHESIVE
BOND LINE OF TITANIUM LAP SHEAR SAMPLES
BONDED WITH EXPERIMENTAL NR-150 ADHESIVES
(20X MAGNIFICATION)

SAMPLES TESTED AT R.T.
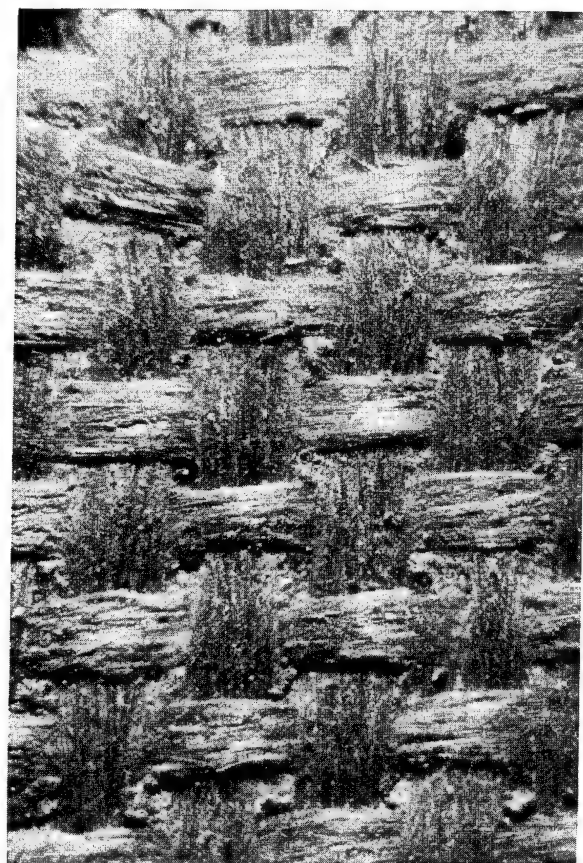
91-3	SAMPLE #	53-L
NMP	SOLVENT	DIGLYME
7.6%	USED PREPREG VOLATILES	9.2%
29.10 MPa	R.T. LAP	22.22 MPa
(4221 psi)	SHEAR STRENGTH	(3222 psi)
ADHESIVE	FAILURE MODE	COHESIVE

ADHESIVE COMPOSITION: 1:1 6FTA:DIAMINE, 60/40 PPD/ODA,
48 WT. % IN SOLVENT CONTAINING
65% ALUMINUM POWDER.

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FIGURE 15

PHOTOMICROGRAPHS OF THE FAILED ADHESIVE
BOND LINE OF TITANIUM LAP SHEAR SAMPLES
BONDED WITH EXPERIMENTAL NR-150 ADHESIVES
(20X Magnification)

SAMPLES TESTED AT 589 K (600°F)

92-2	SAMPLE #	53-2
NMP	SOLVENT USED	DIGLYME
7.6%	PREPREG VOLATILES	9.2%
1.21 MPa (125 psi) COHESIVE	589 K LAP SHEAR STRENGTH FAILURE MODE	12.32 MPa (1787 psi) COHESIVE

ADHESIVE COMPOSITION: 1:1 6FTA:DIAMINE, 60/40 PPD/ODA,
48 wt. % IN SOLVENT CONTAINING
65% ALUMINUM POWDER.

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Comparison of the failed surfaces of lap shear samples tested at 589 K (600°F) also shows significant differences between adhesive bonds made using solutions based on the two solvents. Cohesive failure occurs with both adhesives. In the case of NMP sys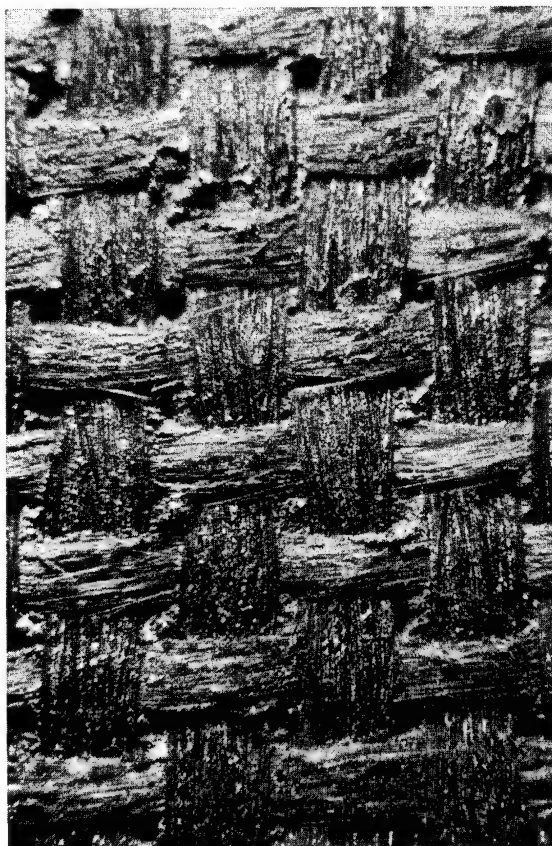tems, the test temperature of 589 K is above the Tg (glass transition temperature) of the adhesive, resulting in a low shear strength resin having a soft, taffy-like consistency at the test temperature. The picture on the left of Figure 15, therefore, shows mounds of solidified resin covering the glass scrim carrier with many holes or voids (dark areas) at the cross-points of the glass fabric.

The picture on the right in Figure 15 showing the failure surface of an adhesive bond made with diglyme solutions is very similar to that on the right of Figure 14. As the Tg of the resin is well above the test temperature (589 K), the bond strength is high (12.32 MPa, 1287 psi), and only a few holes or voids (dark areas) are observed in the adhesive bond line.

From these pictures, it can be inferred that there is a higher void content in adhesive bond lines prepared from the NMP solutions than the diglyme solution, although the adhesive prepreg based on diglyme has a higher volatile level. The voids or holes present in the bond lines prepared from NMP systems in Figures 14 and 15 are believed not to have been generated during the testing of the lap shear sample, but are formed during the bonding process. If a failed sample similar to that in Figure 14 bonded using NMP solutions is lightly sanded to remove the outer adhesive layer, other voids or holes are observed in the interstices of the fabric. Moreover, a free standing air post cure at temperatures above 589 K causes a significant swelling of the bond line of a lap shear sample prepared using NMP solutions, whereas no measurable bond line swelling occurs with lap shear bonds made using diglyme solutions. These facts suggest that adhesive bonds prepared using adhesives based on NMP solutions have higher void levels and higher concentration of volatiles than do bond lines prepared

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using adhesives based on diglyme. It can only be inferred that
the solvent is more readily evolved and the adhesive bond line
more easily consolidated with diglyme based adhesives than with
NMP adhesives.

7. BONDING COMPOSITE ADHERENDS

The initial experiments bonding composite adherends using NR-150 adhesive solutions were carried out using experimental HTS/NR-150B2 unidirectional 1.65-2.29 mm (65-90 mils) thick panels. These panels, supplied by the Space Division, Rockwell International, Downey, California, were thinner and utilized a less stable graphite fiber than that specified by NASA. In order to expedite the program, these panels were used for the first experiments.

The panels were cut into 25.4 mm x 101.6 mm (1" x 4") lap shear coupons and bonded using the procedures used for bonding titanium. The faying surfaces of the composite coupons were lightly sanded first in the direction of the fibers and then in the cross direction, coated with the aluminum filled adhesive solution, and then "B" staged using the procedures in Appendix B, Part I, for NMP solutions and Appendix E for diglyme solutions. Adhesive prepreg was prepared according to the procedures in Appendix D and F for NMP and diglyme solutions, respectively.

Comparison of the results of bonding composite adherends with adhesive prepreg based on NMP and diglyme solutions is given in Table XXI. Three bondings were carried out: two using NMP solutions, one of which was air post cured, and one using a diglyme solution. Both solutions contained the same resin composition.

It is apparent that the diglyme solution produces higher lap shear strength levels at both R.T. and 589 K than does the NMP solution. In fact, the bonds made using the diglyme solution have strength levels close to the goals desired by NASA - 20.69 MPa (3000 psi) at R.T. and 13.79 MPa (2000 psi) at 589 K. Samples post cured using a slow rate of temperature rise had 589 K bond strengths of only 7.83 MPa (1136 psi) significantly below that for samples that were not post cured.

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TABLE XXI

BONDING EXPERIMENTAL HTS/NR-150B2 LAP SHEAR COUPONS NR-150 ADHESIVE COMPOSITIONS[1]

Adhesive Solution Solvent	Bonding Conditions			Post Cure Conditions			Bond Line Thick mm (Mils)	Lap Shear Strength		Remarks
	Time Hours	Temp. K (°F)	Pressure MPa (psi)	Time Hours	Atmosphere	Temp. K (°F)		R.T. MPa (psi)	589K(600°F) MPa (psi)	
NMP	1/2	589 (600)	1.38 (200)	1	Vacuum	589 (600)	.127 (5.0)	16.00 (2320)	-	Composite failure
NMP	1/2	589 (600)	1.38 (200)	1	Vacuum Followed By Air	589 (600) 431→662 (316→732)	.178 (7.0)	15.55 (2255)	7.83 (1136)	Cohesive failure 15% increase in bond line thickness on air post cure
Diglyme	1	589 (600)	1.38 (200)	1	Vacuum	589 (600)	.089 (3.5)	20.46 (2970)	13.45 (1950)	Composite failure at R.T. partial adhesive, cohesive, and composite failure at 589 K

Panels autoclave molded by Rockwell International, Space Division, Downey, California

Adhesive Prepreg: .32 mm (12 1/2 mils) thick, 9.2% volatiles

[1] Adhesive composition: 1:1 6FTA*diamine, 60/40 PPD*/ODA*, 48 wt. % in indicated solvent containing 65 wt. % aluminum powder (based on total cured solids)

It appears from this initial evaluation that bonding composites with adhesives based on diglyme solutions gives the same dramatic result as bonding titanium. Bonding composites with prepreg based on NMP solutions was, therefore, not explored further.

7.1 EFFECT OF POST CURE

Composite lap shear samples based on diglyme solutions of two different NR-150 compositions have been post cured and aged up to 125 hours free standing in air. During the course of this evaluation, composite panels were received from Rockwell International, Space Division, which met the NASA specifications, e.g., unidirectional "Modmor" II/NR-150B2 laminates 3.175 mm (1/8") thick. Therefore, both the thinner HTS/NR-150B2 panels as well as the "Modmor" II panels were bonded and evaluated.

Two different adhesive solution compositions (Compositions E and F, Table XVI) were used for this study. Table XXII, which summarizes the results, is divided into three sections: the top two sections giving the results of bondings and exposing HTS graphite fiber composites using the two different filled adhesive compositions, and the bottom section giving the results of bonding and exposing "Modmor" II graphite fiber composites bonded using prepreg from filled adhesive Composition F.

The conclusions from this study are as follows:

(a) Exposing lap shear samples based on HTS laminates to 589 K air for 450 Ks (125 hours) decreased the 589 K bond strengths by about 15-30% but had little or no effect on the R.T. bond strengths.

(b) Exposing lap shear samples based on "Modmor" II laminates to 589 K air for 450 Ks (125 hours) increased the lap shear strength at both test temperatures.

(c) As most of the failures on testing the lap shear bonds occurred within the composite adherends and not within the adhesive bond line, the observed changes in strength observed are really changes in the composite shear strength. The adhesive strength is,

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TABLE XXII.

EFFECT OF EXPOSURE TO 589 K (600°F) AIR ON LAP SHEAR STRENGTH OF GRAPHITE FIBER/NR-150B2 LAMINATES BONDED WITH EXPERIMENTAL NR-150 ADHESIVES

Fiber Type in Composite	Adhesive Prepreg PPD/ODA Ratio	Thick mm (Mils)	Volatiles %	Air Post Cure Ks Time (Hrs.)	Temp. K (°F)	Bond Line Thickness mm (Mils)	Resin Flow	Lap Shear Strength @ R.T. MPa (psi)	@589K(600°F) MPa (psi)	Failure Mode
HTS	60/40 (Comp. G)	.406 (16)	9.3	None		.279-.381 (11-15)	Slight to Good	15.51 (2249) (1800-2700)	12.25 (1777) (1514-2040)	Within composite at R.T. Within composite and cohesive at 589 K
HTS	"	.406 (16)	9.3	450 (125)	589 (600)	.279-.330 (11-13)	Slight to Good	14.02 (2034) (1812-2256)	8.37 (1212) (1095-1329)	Within composite at R.T. Within composite and cohesive at 589 K
HTS	75/25 (Comp. F)	.356 (14)	12.6	None		.102-.165 (4.0-6.5)	Excessive	17.98 (2608) (2582-2634)	13.02 (1889) (1862-1915)	85% in composite at R.T. 50% in composite at 589 K
HTS	"	.356 (14)	12.6	450	589 (600)	.114-.140 (4.5-5.5)	Excessive	17.94 (2602) (2532-2682)	11.04 (1600) (1520-1678)	Within composite at R.T. cohesive at 589 K
Modmor II	75/25 (Comp. F)	.356 (14)	10.8	72. (20)	589 (600)	.089-.127 (3.5-5.0)	Good	16.58 (2405) (2309-2501)	13.46 (1951) (1915-1988)	Within composite at R.T. 50% within composite at 589 K
Modmor II	"	.381 (15)	11.0	450 (125)	589 (600)	.076-.127 (3.0-5.0)	Slight to Good	20.22 (2933) (2747-3175)		Within composite
Modmor II	"	.406 (16)	11.0	450 (125)	589 (600)	.102-.140 (4.0-5.5)	Slight to Good		15.53 (2252) (1991-2426)	Within composite

Bonding conditions: .033 K/s (5°F/min.) under full vacuum and 1.38 MPa (200 psi)
Bond 3.6 Ks (one hour) at 589 K (600°F) full vacuum and 1.38 MPa (200 psi)
Hold 3.6 Ks (one hour) at 589 K (600°F) full vacuum only
Cool under full vacuum

Adhesive composition: 1:1 6FTA:diamine; PPD/ODA ratio indicated in Column 3
48 wt. % resin in diglyme; 65 wt. % aluminum powder

Composite Thickness: HTS/NR-150B2, 1.42-1.93 mm (56-76 mils)
Modmor II/NR-150B2; 3.00-3.33 mm (118-131 mils)

therefore, above the reported values.

7.2 PREFERRED ADHESIVE COMPOSITION

Based on the conclusions of the study in Section 7.1, the following adhesive composition was chosen to prepare composite lap shear samples for environmental exposure: Solution Composition F, Table XVI, consisting of a 1:.75:.25 mole ratio of 6FTA: PPD:ODA, 48 wt. % cured resin solids in diglyme, containing 65 wt. % of aluminum powder filler (Reynolds Grade 1-131 atomized) based on total cured solids. This adhesive solution was used to prime composite adherends using the procedure in Appendix E and to prepare adhesive prepreg using the procedure in Appendix F. The samples were prepared using a vacuum bag in a press using the procedure in Appendix G which includes a 57.6 Ks (16 hour) post cure at 589 K free standing in air.

7.3. ENVIRONMENTAL EXPOSURE OF COMPOSITE LAP SHEAR SAMPLES

Lap shear samples based on unidirectional "Modmor" II/NR-150B2 - 3.175 mm (1/8") thick adherends bonded using the adhesive and procedures given in Section 7.2 were exposed to the following environments:

(a) Up to 1800 Ks (500 hours) in 589 K air.

(b) 3024 Ks (35 days) at 322°K (120°F) 95% R.H.

(c) 2937.6 Ks (34 days) immersion at R.T. in JP-4 jet fuel.

(d) 2937.6 Ks (34 days) immersion at R.T. in methylethyl-ketone (MEK).

Four samples each then were tested for lap shear strength at R.T. and 589 K along with controls. Four samples were also tested at 561 K (550°F) after 500 hour exposure to 589 K. The weight loss or gain and the change in total thickness in the bonded area was also measured for each exposed sample.

The results of these exposure tests are given in Tables XXIII, XXIV, XXV, and XXVI, for the four environments. The tables report the individual lap shear strengths, the average (arithmetic) strength, standard deviation, the % change in strength over control, the average % weight change, and the average % change in thickness,

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if any. In almost all cases, except where indicated, the samples
failed within the composite adherend, resulting in the adhesive
bond being stronger than the reported value.

As the lap shear samples were bonded four at a time, several
sets of four were bonded and the samples to be exposed chosen at
random from the total.

7.3.1 Exposure to 589 K (600°F) Air

The results of exposing lap shear samples to 589 K (600°F)
air for 450, 900, and 1800 Ks (125, 250, and 500 hours) are
summarized in Table XXIII. The oven used for this exposure had a
volume of about 2 1/2 liters with a positive air flow through the
oven sufficient to change the air every 10 minutes. Two sets of
control samples were used; one set for the 125 and 250 hour
exposures (Lines 1 and 4, Table I), and one set for the 500 hour
exposure (Lines 7 and 11, Table I). Only three samples were
available for testing at R.T. as the control for the 1800 Ks (500
hour) exposure (Line 7).

In most cases, there was much scatter in the strengths
measured as indicated by the large standard deviations obtained.
As a consequence, any differences in the average lap shear
strengths shown may not necessarily be real. Moreover, as all lap
shear failures occurred within the composite adherends, the effect
of high temperature exposure on the adhesive bond line has not been
measured. With the above qualifications, it may be concluded that
there is little effect on R.T. lap shear strength on exposure of
up to 450 Ks (250 hours) in 589 K air (compare Line 1 with Lines
2 and 3, Table XXIII), but exposure for 1800 Ks (500 hours) may
degrade slightly the R.T. lap shear strengths (compare Lines 7 and
8, Table XXIII). Exposure to 589 K air appears to reduce the 589
K lap shear strengths by 11% after 450 Ks (250 hours) and by 17%
after 1800 Ks (500 hours) (compare Lines 4 with 6 and Lines 11
with 12, Table XXIII). The lap shear samples lost only about 1%
in weight after 1800 Ks (500 hours) exposure to 589 K air.

TABLE XXIII.

589 K (600°F) AIR EXPOSURE
OF COMPOSITE SAMPLES
BONDED WITH NR-150 ADHESIVE

Line	Exposure Ks (Hours)	Test Temp. K(°F)	Lap Shear Strength* MPa (psi)						Decrease in Strength %	Sample Weight Loss Average %
			Sample 1	Sample 2	Sample 3	Sample 4	Average	Standard Deviation		
1	None (Control)	R.T.	11.82 (1714)	16.67 (2418)	16.36 (2373)	17.74 (2573)	15.62 (2270)	2.62 (380)		
2	450 (125)	R.T.	20.18 (2926)	10.74 (1557)	17.67 (2563)	16.28 (2588)	16.26 (2358)	4.00 (580)	N.1	0.26
3	900 (250)	R.T.	12.19 (1768)	16.55 (2401)	21.08 (3058)	13.91 (2017)	15.93 (2311)	3.87 (561)	N.1	0.42
4	None (Control)	589(600)	12.60 (1828)	17.67 (2563)	14.50 (2103)	14.48 (2167)	14.93 (2166)	2.09 (303)		
5	450 (125)	589(600)	14.55 (2110)	10.70 (1552)	18.35 (2661)	15.99 (2319)	14.90 (2361)	5.27 (265)	N.1	0.30
6	900 (250)	589(600)	9.00 (1306)	13.25 (1921)	16.47 (2389)	14.45 (2095)	13.29 (1928)	3.28 (475)	11.0?	0.54
7	None (Control)	R.T.	19.79 (2870)	9.54 (1383)	16.22 (2353)		15.21 (2206)	5.21 (755)		
8	1800 (500)	R.T.	15.99 (2319)	14.34 (2080)	17.02 (2469)	8.14 (1180)	13.87 (2012)	3.98 (577)	9.0?	0.97
9	1800 (500)	561(550)	13.22 (1918)	15.81 (2293)	16.75 (2430)	7.30 (1059)	13.27 (1925)	4.25 (617)		0.71
11	None (Control)	589(600)	16.24 (2356)	16.84 (2443)	17.24 (2500)	16.73 (2426)	16.76 (2431)	0.41 (59)		
12	1800 (500)	589(600)	14.27 (2070)	14.04 (2036)	17.24 (2501)	10.07 (1461)	13.91 (2017)	2.74 (427)	17.0?	0.98

*All samples failed within the composite adherend.

Composite used: 3.175 mm (1/8") thick "Modmor" II/NR-150B2 unidirectional laminates

Adhesive prepreg used: 0.38 mm (15 mils) thick containing 11.5% volatiles, 285% cured resin solids
50% aluminum powder, 11% glass scrim cloth. Based on Composition F, Table XVI.

Samples exposed at least 15 minutes before testing at 589 K.

7.3.2 Exposure to High Humidities

Composite lap shear samples have been exposed to 322 K (120°F) 95% R.H. for 3024 Ks (35 days) with the effect on the R.T. and 589 K (600°F) lap shear strength indicated in Table XXIV. In order to test the effect of the high humidity on the 589 K lap shear strength without an excessive loss of absorbed water, the sample was tested after 7 minutes exposure to 589 K, the time required for a lap shear sample to reach the test oven temperature. The lap shear sample absorbed about 2 weight % water after 35 days exposure which caused a 24% decrease in the R.T. lap shear strength and a 40% decrease in the 589 K lap shear strength. Although failure of the exposed samples occurred within the composite adherends when tested at R.T., three samples tested at 589 K failed partially within the adhesive bond line. The absorbed water, therefore, causes some plasticization of the composite as well as the adhesive bond line, thereby reducing somewhat the strength levels. Analysis of the bond line by the TMA technique even at high heating rates failed to show a decrease in resin Tg brought about by the presence of absorbed water.

The lap shear strength level of 10.53 MPa (1458 psi) at 589 K (600°F) after exposure to the high humidity conditions shows that this adhesive is only slightly affected by these conditions.

7.3.3 Exposure to JP-4 Jet Fuel

After a 2937.6 Ks (34 day) immersion at R.T. in JP-4 jet fuel, the lap shear samples gained over 5 wt. %. However, there was essentially no effect on the R.T. lap shear strength as indicated in Table XXV. The excessive amount of jet fuel absorbed by the lap shear samples precluded testing at 589 K because of the potential fire hazard. TMA analysis of an exposed lap shear bond indicates the adhesive resin Tg of 590 K (601°F) may have been lowered only slightly by the environment. All samples tested, however, failed within the composite adherend, so again, the effect of any of JP-4 jet fuel on the adhesive bond line is not apparent.

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TABLE XXIV.

HIGH HUMIDITY EXPOSURE OF COMPOSITE LAP SHEAR SAMPLES BONDED WITH NR-150 ADHESIVE

Exposure Conditions	Test Temp.	Lap Shear Strength MPa (psi)					Standard Deviation	Decrease in Strength %	Sample Weight Increase Ave. %	Sample Thickness Increase Ave. %
		Sample 1	Sample 2	Sample 3	Sample 4	Average				
R.T. Air Control	R.T.	17.83 (2586)	18.14 (2631)	17.70 (2567)	16.98 (2462)	17.66 (2562)	0.49 (71)			
3024 Ks (35 days) at 22 K (120°F) 95% R.H.	R.T.	12.20 (1770)	16.40 (2379)	12.19 (1768)	13.25 (1921)	13.51 (1959)	1.99 (289)	24.0	2.09	NIL
R.T. Air Control	589(600)	16.21 (2551)	16.79 (2435)	16.80 (2437)	17.72 (2570)	16.88 (2448)	0.63 (91)			
3024 Ks (35 days) at 22 K (120°F) 95% R.H.	589(600)	8.15* (1182)	9.09* (1319)	11.55 (1675)	11.75* (1704)	10.53 (1458)	1.52 (220)	40.0	2.00	NIL

*Samples failed cohesively within adhesive bond line.

All other samples failed within the composite adherend.

Samples tested at 589 K (600°F) were conditioned for .42 Ks (7 mins.) before test was started.

TABLE XXV.

JP-4 JET FUEL EXPOSURE OF
COMPOSITE LAP SHEAR SAMPLES
BONDED WITH NR-150 ADHESIVE

Exposure Conditions	Test Temp.	Lap Shear Strength MPa (psi)						Decrease in Strength %	Sample Weight Increase Ave. %	Sample Thickness Increase Ave. %
		Sample 1	Sample 2	Sample 3	Sample 4	Average	Standard Deviation			
R.T. Air Control	R.T.	12.19 (1768)	19.37 (2810)	24.44 (3545)	20.04 (2907)	18.98 (2752)	5.07 (736)			
2937.6 Ks (34 days) in 24 jet fuel at R.T.	R.T.	16.31 (2365)	20.17 (2926)	20.25 (2937)	17.22 (2497)	18.49 (2681)	2.03 (294)	NIL	5.11	0.6
R.T. Air Control	589(600)	13.71 (1988)	15.26 (2213)	14.65 (2125)	16.80 (2437)	15.10 (2191)	1.30 (188)			
2937.6 Ks (34 days) in 24 jet fuel at R.T.	589(600)	N O T T E S T E D								

All failures occurred within composite adherends.

7.3.4 Exposure to Methylethylketone

After a 2937.6 Ks (34 day) immersion of lap shear samples in methylethylketone (MEK) at R.T., the samples gained almost 10 wt. % and there was a noticeable increase in thickness (swelling) of about 4.1% in the overlap area. However, the significant absorption of MEK did not significantly degrade the R.T. lap shear strengths as indicated in Table XXVI. In two out of the four exposed samples tested, failure partially occurred within the adhesive bond line. TMA analysis of the bond line of an exposed sample indicated a reduction in the resin Tg as the sample blew apart at 520 K (476°F).

7.4 WIDE AREA BONDING

An investigation of wide area bonding using the diglyme based NR-150 adhesive system was carried out. Initially, wide area bonds were prepared with composite adherends in a press using simulated autoclave conditions. Finally, larger area bonded panels were prepared using an autoclave.

7.4.1 Press Bonding

Previous to preparing the wide area bonds using an autoclave, scouting work was carried out on smaller (.1524 m x .1524 m, 6" x 6") wide area composite panels using simulated autoclave conditions in a press. The various bonding conditions used and the results of lap shear tests carried out on samples cut from the wide area bonds are given in Table XXVII. The following four conditions were used to prepare the wide area bonds: the conditions used to prepare lap shear samples - one hour at full vacuum 200 psi followed by one hour under full vacuum only and then a post cure at 589 K (Sample 155); bonding using a longer time at 589 K (600° F) under vacuum only followed by a post cure to 616 K (650°F); bonding for four hours at 589 K with no post cure (Sample 51); and bonding for three hours at 589 K followed by a post cure to 644 K (700°F).

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TABLE XXVI.

METHYLETHYLKETONE (MEK) EXPOSURE
OF COMPOSITE LAP SHEAR SAMPLES
BONDED WITH NR-150 ADHESIVE

Exposure Conditions	Test Temp.	Lap Shear Strength MPa (psi)						Decrease in Strength %	Sample Weight Increase Ave. %	Sample Thickness Increase Ave. %
		Sample 1	Sample 2	Sample 3	Sample 4	Average	Standard Deviation			
R.T. Air Control	R.T.	16.71 (2424)	18.36 (2663)	18.46 (2678)	19.57 (2838)	18.28 (2651)	1.17 (170)			
2937.6 Ks (34 days) in MEK at R.T.	R.T.	14.65* (2125)	16.54* (2399)	17.25 (2502)	19.53 (2833)	17.00 (2465)	2.02 (293)	NIL	9.8%	4.1%
R.T. Air Control	589(600)	15.30 (2219)	16.40 (2379)	16.69 (2420)	15.74 (2283)	16.03 (2325)	0.63 (91)			
2937.6 Ks (34 days) in MEK at R.T.	589(600)	N O T T E S T E D								

*These samples failed partly cohesively within the adhesive bond line.

All other samples failed within composite adherend.

TABLE XXVII.

WIDE AREA (.124 m x .124 m, 6" x 6") BONDING OF COMPOSITES USING DIGLYME BASED NR-150 ADHESIVE USING A PRESS

Sample #	Bonding Conditions Under Full Vacuum			Air Post Cure		Lap Shear Strength			Failure Mode	TMA Analysis	
	Time Hours	Temp. K (°F)	Pressure MPa (psi)	Time Hours	Temp. K (°F)	Sample Position in 6" x 6" Bond	Test Temp. K	MPa (psi)		Onset Temp. K(°F)	Tg K(°F)
F	1	589 (600)	1.38 (200)	16	589 (600)	outside	R.T.	24.00 (3481)	within composite	571(568)	575(576)
	1	589 (600)	zero			inside	589	11.57 (1678)	cohesive in bond line		
						middle	R.T.	8.29 (1203)	cohesive in bond line		
						inside		Not Tested			
						outside	R.T.	16.82 (2439)	within composite		
G	1	589 (600)	1.38 (200)	16	589 (600)	inside	R.T.	16.87 (2447)	within composite	–	585(594)
	4	589 (600)	zero	8	603 (625)	inside	589	17.80 (2581)	within composite		
				16	616 (650)	middle	R.T.	9.65 (1400)	cohesive in bond line		
						inside	589	4.53 (657)	cohesive in bond line		
						outside		Not Tested			
H	4	589 (600)	1.38 (200)	None	None	outside	R.T.	13.50 (1958)	within composite	503(441)	520(478)
						inside	R.T.	19.59 (2841)	within composite	523(482)	540(511)
						middle	R.T.	14.70 (2133)	within composite		
						inside		Not Tested			
						outside	R.T.	24.81 (3598)	within composite		
I	3	589 (600)	1.38 (200)	16	533 (500)	outside	R.T.	14.54 (2109)	cohesive in bond line	583(590)	595(612)
				8	561 (550)	inside		Not Tested			
				16	589 (600)	middle	R.T.	2.83 (411)	cohesive in bond line		
				23	616 (650)	inside	R.T.	9.05 (1313)	"		
				21	630 (675)	outside	R.T.	9.00 (1305)	"		
				8	644 (700)						

Simulated autoclave conditions using a press: 2 K/min. rate of temperature rise under full vacuum and 1.38 MPa (200 psi).

Adhesive prepreg .203 mm (8 mils) thick containing 10% volatiles, 24% cured resin, 45% aluminum powder, 21% scrim.

Adhesive solution composition - 1:1 6FTA*:diamine; 75/25 PPD*:ODA; 48 wt. % resin solids in diglyme – containing 65% aluminum powder.

Composites: "Modmor" II/NR-150B2 unidirectional laminates, 3.175 mm (1/8") thick.

*6FTA: 2,2 bis(3',4'-dicarboxyphenyl) hexafluoropropane; PPD: paraphenylenediamine; ODA: oxydianiline

Five lap shear samples were then cut out of the middle of the wide area bonded panels with the middle sample always tested at R.T. and the others tested either at R.T. or 589 K. A summary of the results shown in Table XXVII is as follows:

(1) Post curing at temperatures from 589 K (600°F) to 644 K (700°F) results in low bond strengths for the middle lap shear sample with failure occurring cohesively within the adhesive (compare middle samples from wide area bonds F, G, and I, Table XXVII).

(2) Only when post cure is not used is the bond strength of the middle sample at the levels approaching that desired and is the adhesive bond stronger than the composite (middle sample from wide area bond H, Table XXVII). During post cure, the trapped volatiles swell the bond line producing a porous weak bond.

(3) The glass transition temperature of the adhesive bond near the center of the wide area bond is below the desired minimum 589 K in all cases except the sample post cured to 644 K (700°F). However, post curing to this temperature severely degrades the R.T. bond strength (Sample I, Table XXVII).

From this work preparing wide area bonds in a press, it was concluded that: (1) A longer bonding time under pressure was required to produce good bonds in the center of a bonded panel. (2) Post curing should not be used unless the removal of a sufficient amount of volatiles was accomplished during the bonding step. (3) Bonding at higher temperatures, for example, 616 K (650°F), may give increased R.T. bond strengths in the center of a wide area bond and result in acceptable 589 K strengths without requiring a post cure. These conclusions were considered on determining the conditions to be used for bonding the wider panels (.254 m x .254 m, 10" x 10") in the autoclave.

7.4.2 Autoclave Bonding

Four wide area (.254 m x .254 m, 10" x 10") bonded panels were prepared using an autoclave at Rockwell International, Space Division. Three of the bonded panels were prepared using

"Modmor" II/NR-150B2 unidirectional 3.175 mm (1/8") thick
adherends and the adhesive system used for preparing lap shear
samples for the environmental exposure tests. The fourth wide
area bonded panel was made using 6-4 titanium 1.016 mm (40 mils)
thick adherends. The composite adherends were surface treated and
primed as indicated in Appendix E and the titanium panels were
etched with "Pasajell" 107 and primed as indicated in Appendix A.
The adhesive prepreg for the wide area bonds was prepared using
the procedure described in Appendix G.

The titanium bonded panel and one composite bonded panel
were bonded in an autoclave using the following procedure: heat
from R.T. to 589 K (600°F) at 2.8 Ks (5°F)/min. under full vacuum
and 200 psi; hold at 589 K for 21.6 Ks (six hours) under full
vacuum and 200 psi; cool to 339 K (150°F) under full vacuum and
200 psi. The two other composite panels were bonded under
similar conditions at 616 K (650°F) and held at that temperature
for 21.6 Ks (six hours) before cooling.

Ultrasonic C-scans of the bonded panels at 10 MHz indicated
that the titanium and composite panels bonded at 589 K (600°F)
had low void levels in the center of the panels with some poorly
bonded areas near the edge. The two composite panels bonded at
616 K (650°F) showed almost no poorly bonded areas by the C-scan
technique. The titanium panel and the composite panel bonded at
589 K and one composite panel bonded at 616 K were cut into seven
25.4 mm (1" wide) 12.7 mm (1/2") overlap lap shear samples from
the middle area of each panel. The middle lap shear sample was
from the middle of the panel.

The bond lines of the lap shear samples cut from the
titanium wide area bonded panel were only about .254 mms (10 mils)
thick but contained numerous voids. As the lap shear samples cut
from the middle of the panel could be readily pulled apart by hand,
no tests were made on these samples. It is apparent from these
findings that the ultrasonic equipment used to make the C-scans
was not sufficiently sensitive to pick up the voids in the bond
lines.

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This result using adhesive based on diglyme is similar to that found on wide area bonding titanium using NMP solutions in Section 4.8. It is concluded that the preparation of acceptable wide area bonds using titanium adherends will require an adhesive system containing a lower solvent content and/or a more volatile solvent, and processing conditions using longer times and higher temperatures.

Lap shear samples were also cut out of the .254 m x .254 m wide area bonds made with composite adherends. Visual inspection of the bond lines prepared at either temperature indicated that thin (.254 mm, 10 mil) low void bonds were in the center of both bonded panels. Photographs of the edge of the bond line of the lap shear sample cut from the center of the wide area sandwich panel bonded for 21.6 Ks (6 hours) at 616 K (650°F) are shown in Figure 16. These photographs clearly show threads from the glass scrim cloth but very few voids.

The results of lap shear strength tests on the samples bonded using composite adherends are given in Table XXVIII. The bonds were tested at both R.T. and 589 K, but the lap shear sample cut from the centers of both wide area panels were tested at R.T.

In general, the results in Table XXVIII indicate a better bond was formed in the center of the wide area bonds when the higher bonding temperature of 616 K (650°F) was used. The lap shear samples tested at room temperature and bonded at 616 K all failed within the composite adherends, while some of the samples bonded at 589 K failed within the adhesive. Of the samples tested at 589 K (although not from the center area of the wide area bonds), the ones bonded at 616 K had bond strengths approaching the NASA goal level of 13.79 MPa (2000 psi).

Examination of the bond area of the tested lap shear sample from the center of panel bonded at 616 K not only indicates some failure in the composite, but also shows voids randomly distributed throughout the adhesive bond.
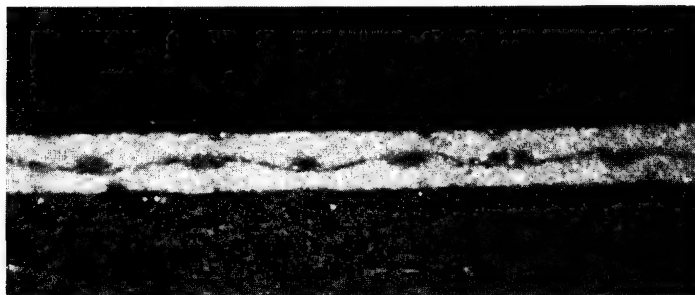
FIGURE 16

PHOTOGRAPHS OF EDGE OF BOND LINE
OF LAP SHEAR SAMPLE CUT
FROM THE CENTER OF A .254 m x .254 m
(10" x 10") WIDE AREA BOND

(Composite adherends bonded with
adhesive solution composition F Table 16)

Bond Line in Overlap Area (6X)
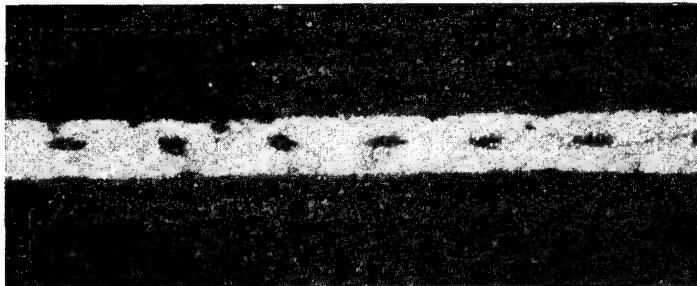
Bond Line Near Overlap Area (25X)

Bond Line in Another Area (25X)
Near the Overlap

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TABLE XXVIII

LAP SHEAR STRENGTH OF SAMPLES CUT
FROM WIDE AREA BONDS

.254 m x .254 m (10" x 10") Wide Area Bonds
Autoclave Bonded Using Composite Adherence
and Experimental NR-150 Adhesive Solution Containing Diglyme

Autoclave Bonding Temperature	Position of Lap Shear Sample in Wide Area Bond	Test Temperature K (°F)	Lap Shear Strength MPa (psi)	Failure Mode	Bond Line Tg K (°F)
589 K (600°F)	Outside (50.8 mm from edge)	R.T.	11.10(1610)	Within Adhesive	
	Next to Center Center	R.T. R.T.	13.10(1901) 4.34 (630)	Within Composite Within Adhesive	581 (586)
	Next to Outside Outside (50.8 mm from edge)	589 (600) 589 (600)	1.68 (244) 7.18(1042)	Within Adhesive Within Adhesive	
616 K (650°F)	Outside (50.8 mm from edge)	R.T.	9.93(1440)	Within Composite	
	Next to Center Center	R.T. R.T.	10.66(1546) 13.19(1913)	Within Composite Within Composite	558 (545)
	Next to Outside Next to Outside (76.2 mm from edge)	589 (600) 589 (600)	12.17(1765) 13.75(1994)	Within Adhesive Within Adhesive	

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It is concluded from this work on the wide area bonding using NR-150 adhesive solutions that:

(1) Better bonds are obtained on bonding composites than on bonding titanium.

(2) Better bonds are formed on bonding at 616 K (650°F) than when bonding at 589 K (600°F).

(3) Wide area bonding using systems containing diglyme does not produce void free bond lines on bonding for 21.6 Ks (6 hours), 616 K (650°F), at 1.38 MPa (200 psi) in an autoclave.

(4) Adhesive systems containing volatiles having a higher vapor pressure and a lower voiling point than diglyme (b.p. 435 K, 324°F) should produce better quality bonds.

(5) The selected experimental NR-150 adhesive solution, which produces acceptable lap shear bonds (Composition F, Table XVI containing aluminum powder), does not produce wide area bonds which meet the NASA goal levels.

Further effort should be directed toward the scouting of solvents suitable for NR-150 adhesive compositions which have higher volatility than diglyme and, therefore, diffuse more readily out of a wide area bond line.

8. TITANIUM HONEYCOMB FACE SHEET
SANDWICH PANELS

One of the final tasks in the contract was to prepare sandwich panels 63.5 mm x 63.5 mm (2 1/2" x 2 1/2") from "Modmor" II/NR-150B2 6 ply cross ply laminates and a 25.4 mm (1") high titanium honeycomb bonded with the preferred NR-150 adhesive. These were evaluated in a flatwise tensile test at R.T. and 589 K initially and after 1800 Ks (500 hours) exposure to 589 K.

The flatwise tensile specimens were prepared using .965 mm (38 mil) cross ply laminates prepared by Rockwell International, Space Division, Downey, California, and 25.4 mm (1") thick square cell (6.35 mm x 6.35 mm (1/4" x 1/4")) perforated titanium honeycomb supplied by NASA. The composite face sheets were primed using the procedure in Appendix E with Solution F, Table XVI, containing 65% aluminum powder. Both edges of the titanium honeycomb were "Pasajell" 107 etched using the procedure in Appendix A omitting the "sandblast" step. The edges of the etched honeycomb were then dipped into the warmed aluminum filled adhesive solution and "B" staged according to Appendix E, Step 4.

As suggested by NASA, adhesive prepreg used for preparing lap shear samples was then used to bond the primed composite face sheets to the primed titanium honeycomb core.

Autoclave conditions in a press similar to those in the procedure in Appendix G were used to bond the panels. For these honeycomb samples, a maximum pressure of .34 MPa (50 psi) was used during the bonding operation.

Adaptors for testing were bonded on the honeycomb sandwich face sheets with an industrial two-part room temperature curing epoxy adhesive for testing at R.T. For testing at 589 K, aluminum-filled NR-150 adhesive solution Composition F, Table XVI, was used to bond the adaptors. This adhesive was used to prime the SS adaptors and the face sheet surfaces. Adhesive prepreg based on this same adhesive solution was used to bond the adaptors on both sides of the honeycomb sandwich simultaneously using a press (no

vacuum bag) bonding for two hours at 589 K, .34 MPa (50 psi).

The results of tests shown in Table XXIX on these honeycomb sandwich panels were disappointing. Two of the samples failed cohesively within the composite face sheet and two failed at the honeycomb cell edge/adhesive prepreg interface. All samples had poor flatwise tensile strengths.

Visual examination of the samples that failed at the honeycomb cell edge showed two problems: In one sample, the primer coating had flowed away from the cell edge. In the other sample, the fillet that was formed was porous and full of bubbles. From these observations, it is obvious that the primer coating on the honeycomb cell edge must be cured to a much lower volatile level to give a non-porous fillet and to prevent the primer from flowing away from the cell edge.

As two of the flatwise tensile specimens failed cohesively within the graphite fiber/polyimide face sheets, it has to be assumed that the face sheet panels were not of high quality. Although visual inspection of the edge of the panel using a microscope does not show many voids, poor fusion between the prepreg layers could account for this failure. Mechanical tests on the cross ply panels should show lower than desired property levels.

TABLE XXIX

FLATWISE TENSILE STRENGTH OF COMPOSITE FACE SHEET/TITANIUM
HONEYCOMB SANDWICH PANELS

| Sample History	Test Temperature K (°F)	Flatwise Tensile Strength MPa (psi)	Failure Mode
As Prepared	R.T.	.74 (108)	Adhesive between face sheet and honeycomb cell edge
After 1800 KS (500 hours) exposure to 589 K (600°F) air	R.T.	.93 (135)	Cohesive within composite face sheet
As Prepared	589 (600)	.19 (27)	Cohesive within composite face sheet
After 1800 KS (500 hours) exposure to 589 K (600°F) air	589 (600)	.35 (51)	Adhesive between face sheet and honeycomb cell edge

9. CRACK PROPAGATION TESTS

To determine the toughness of the preferred NR-150 adhesive composition (Composition F, Table XVI), the standard wedge crack propagation test[14] was carried out using composite adherends bonded with aluminum filled adhesive. "Modmor" II/NR-150B2 unidirectional laminates 3.175 mm (1/8") thick and 25.4 mm (1") wide by 152.4 mm (6") long were surface primed over 139.7 mms (5 1/2") of their length. The coupons were then bonded using the procedure in Appendix G with adhesive prepreg as prepared in Appendix F. The specimens were, therefore, bonded over only 139.7 mms of their length. A SS wedge 25.4 mm x 25.4 mm x 3.175 mm (1" x 1" x 1/8") which is pointed on one edge is inserted into the unbonded space between the laminates and the length of the resulting crack in the adhesive measured after exposure to 589 K (600°F) for various times[15].

The result of this test is given in Figure 17. It is observed that although the initial crack length is long (over 50.8 mm) because of the high stress levels brought about by the stiff composite adherends, no increase in crack length occurred up to 259 Ks (72 hours), the duration of the test. This result is attributed to the toughness of the adhesive resin having a high degree of thermoplasticity.

FIGURE 17

EVALUATION OF ADHESIVE CRACK PROPAGATION
AT 589K (600°F) USING
THE WEDGE CRACK PROPAGATION TEST
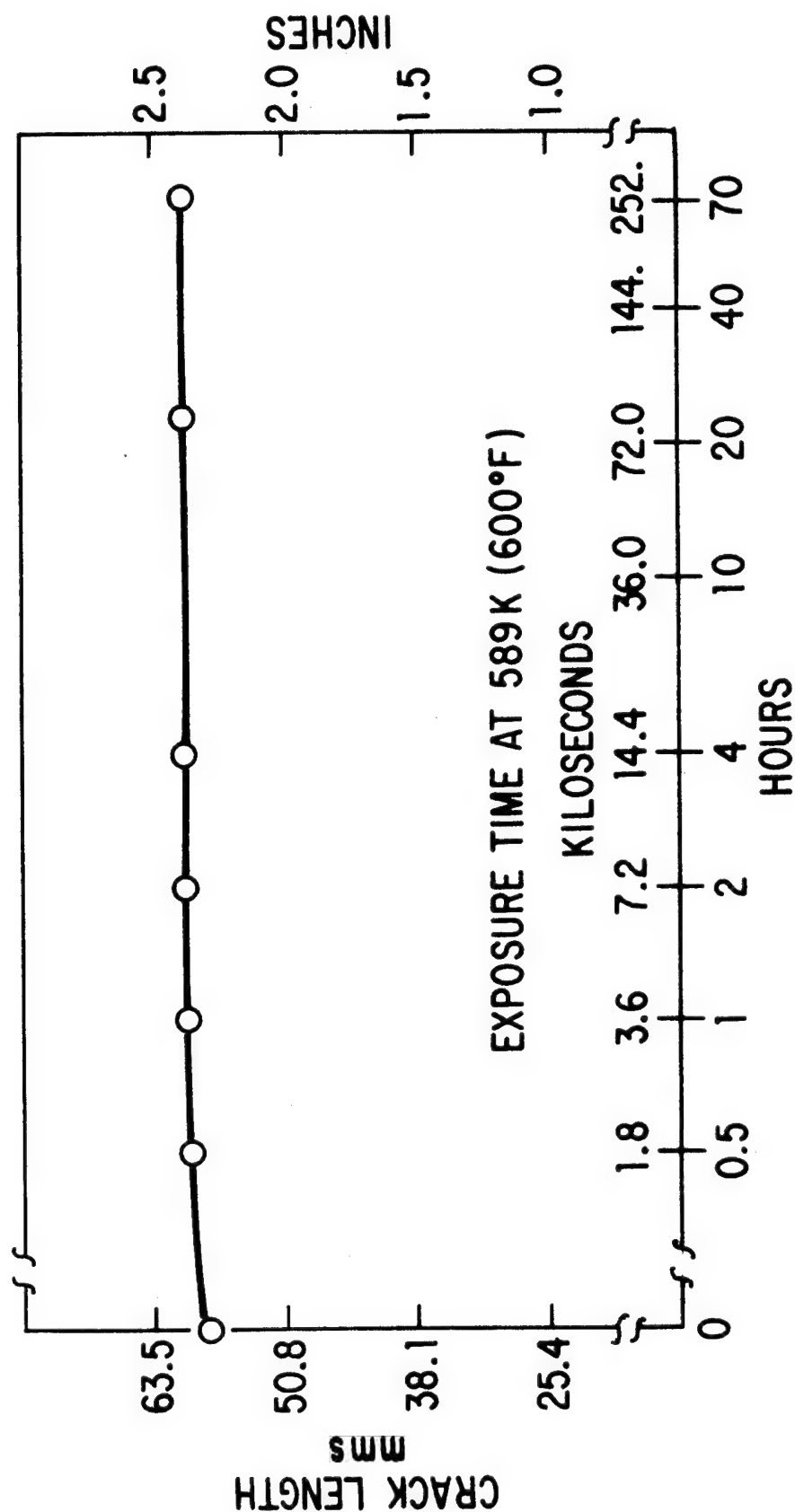
10. PROPERTIES OF COMPOSITE PANELS

The composite lap shear and wide area bonded samples have been prepared from six .279 m x .787 m (11" x 31") 3.175 mm (1/8") thick panels supplied by Rockwell International, Space Division. These panels were molded from "Modmor" II/NR-150B2 unidirectional prepreg using an autoclave at a maximum temperature of 589 K (600°F). The panels were then post cured by Rockwell up to 672 K (750°F). The panels were each received in two pieces: a .279 m x .229 m (11" x 9") section and a .279 m x .533 (11" x 21") section. Lap shear coupons (25.4 mm x 101.6 mm, 1" x 4"), panels for wide area bonding (.152 m x .152 m, 6" x 6"), and mechanical test specimens were cut out of the panels in a random pattern. The specimens included flex bars (12.7 mm x 101.6 mm, 1/2" x 4"), short beam shear samples (6.35 mm x 33.87 mm; 1/4" x 3/4"), and samples for TMA and TGA determination. Before being used, all of the samples were dried in air at 473 K (392°F) for at least 16 hours. Random lap shear coupons checked from each panel had weight losses in the range of 0.65% to 1.00% on drying.

The properties of the test specimens obtained from these panels are given in Table XXX. The panel densities are obtained by weighing the large panel section and measuring its dimensions as received. The resin Tg and onset temperature were obtained by TMA and the volatile content and resin content were measured by TGA in nitrogen. The mechanical properties were measured at both R.T. and 589 K (600°F) with the average of 3 to 11 samples, chosen from different areas of the panels, reported.

In general, the mechanical properties of the panels were disappointingly low.* Flex strengths of 13.79 MPa (200 K psi) and

*These properties were associated with poor quality laminates prepared by a then-inexperienced vendor. In the following Section 11, results with better quality, later laminates are discussed.

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TABLE XXX.

PROPERTIES OF UNIDIRECTIONAL "MODMOR" II/NR-150B2 COMPOSITE PANELS
USED FOR THE PREPARATION OF LAP SHEAR SAMPLES

1 Panel # Rockwell International	Du Pont 14964-	2 Panel Dimensions Meters (Inches)	3 Density g/cc	4 TMA Analysis Onset Temp. K (°F)	Tg K (°F)	5 TGA Analysis Volatiles Remaining %	6 Resin Content %	7 Thickness Range mm (Mils)	8 Test Temp. K (°F)	9 Flex Strength MPa (K psi)	10 Flex Modulus GPa (M psi)	11 Short Beam Shear Strength MPa (K psi)
1722-1A-1/8	20H	.279x.533 (11x21)	1.475	613 (644) — —	625 (666) 618 (653) 620 (656)	0.65	46-48	2.79-3.35 (110-132)	R.T.	899.9 (130.5) (3 samples)	104.8 (15.2) (3 samples)	31.0 (4.5) (10 samples)
									589 (600)	607.8 (88.1) (3 samples)	106.9 (15.5) (3 samples)	26.9 (3.9) (10 samples)
1722-1B-1/8	58A	.279x.533 (11x21)	1.50	608 (635) 613 (644) —	620 (656) 623 (662) 636 (686)	0.55	41-56	2.56-3.15 (101-124)	R.T.	528.9 (76.71) (5 samples)	104.7 (15.18) (5 samples)	26.34 (3.82) (10 samples)
	58H	.229x.279 (9x11)							589 (600)	498.9 (72.36) (5 samples)	101.9 (14.78) (5 samples)	20.89 (3.03) (10 samples)
1722-1C-1/8	58B	.279x.533 (11x21)	1.44	623 (662) — 638 (689)	635 (684) 628 (671) 650 (710)			2.67-3.25 (105-128)	R.T.	697.6 (101.18) (4 samples)	105.8 (15.24) (4 samples)	27.17 (3.94) (10 samples)
	58I	.229x.279 (9x11)							589 (600)	524.8 (76.11) (5 samples)	100.3 (14.55) (5 samples)	23.24 (3.37) (10 samples)
1722-2A-1/8	58C	.279x.533 (11x21)	1.43	618 (653) 615 (648) —	625 (666) 621 (658) 621	0.7-0.9	35-45	2.67-3.53 (105-139)	R.T.	797.3 (115.64) (5 samples)	105.4 (15.28) (5 samples)	31.10 (4.51) (10 samples)
	58J	.229x.279 (9x11)							589 (600)	592.0 (85.86) (5 samples)	101.3 (14.69) (5 samples)	26.13 (3.79) (11 samples)
1722-2B-1/8	58D	.279x.533 (11x21)	1.42	618 (653) —	626 (628) 625 (666) 625 (666)	0.7-0.85	30-46	2.79-3.10 (110-122)	R.T.	653.6 (94.80) (5 samples)	107.3 (15.56) (5 samples)	26.82 (3.89) (10 samples)
	58K	.229x.279 (9x11)							589 (600)	523.2 (75.88) (5 samples)	102.5 (14.87) (5 samples)	21.03 (3.05) (9 samples)
1722-2C-1/8	58E	.279x.533 (11x21)	1.36	— — —	628 (671) 631 (676)			2.62-3.28 (103-129)	R.T.	702.1 (101.88) (5 samples)	106.8 (15.49) (5 samples)	26.20 (3.80) (10 samples)
	58K	.229x.279 (9x11)							589 (600)	473.0 (68.60) (5 samples)	100.9 (14.64) (5 samples)	20.69 (3.00) (10 samples)

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beam shear strengths of 689.95 MPa (10 K psi) at R.T. were
expected. This is to be contrasted with the 528.9 MPa (76 K psi)
to 899.8 MPa (130.5 K psi) flex strengths and 26.2 MPa (3.8 K psi)
to 31.1 MPa (4.51 K psi) short beam shear strengths obtained at
R.T. In some panels, there was a large variation in resin content
across the panel (see Panel 58D, Column 6, Table XXX). The failure
of the lap shear samples within the composite adherends at R.T. at
strength levels lower than desired is probably the result of the
poor mechanical properties of the panels.

    The excessive absorption of jet fuel and MEK by the lap shear
samples, as discussed in Sections 7.3.3 and 7.3.4, is believed to
result partly from the poor quality of the composite adherends
which have lower than desired mechanical properties. Representa-
tive micrographs of the cross section of two areas of a "Modmor"
II/NR-150B2 unidirectional panel used for the lap shear adherends
are shown in Figure 18. The many cracks in the thickness direction
of the panel are to be observed in the upper micrograph which was
taken from an area of the panel for which analysis using the
ultrasonic C scan technique indicated the presence of voids. These
voids may be partly responsible for the high levels absorbed by
the lap shear samples when immersed in jet fuel and MEK.

    Although the composite panels used for the bond studies were
poorer in quality than that desired, the time constraints imposed
by the contract prevented the procurement of better quality panels.
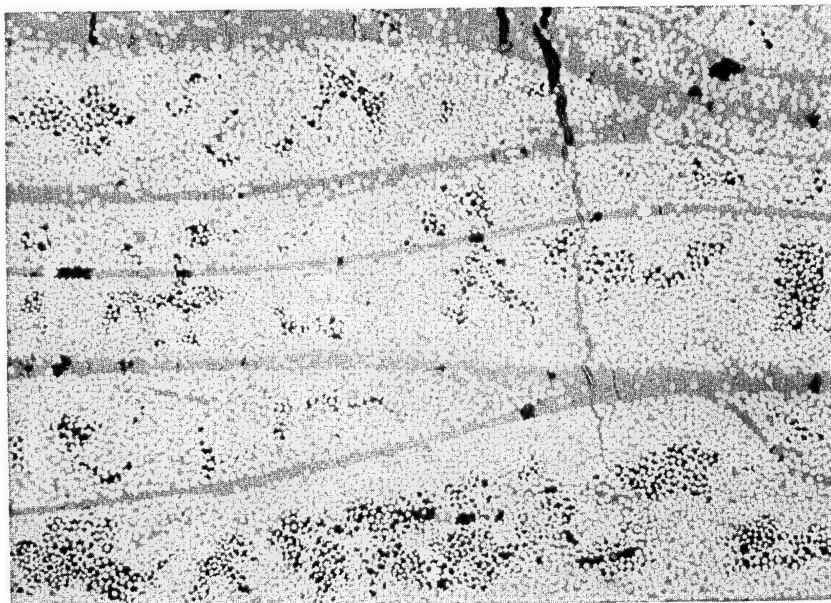
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FIGURE 18

PHOTOMICROGRAPHS OF
CROSS-SECTIONS FROM "MODMOR" II/NR-150B2
COMPOSITE 3.175 mm (1/8") THICK PANELS USED
AS ADHERENDS FOR BONDING STUDIES

(100X MAGNIFICATION)
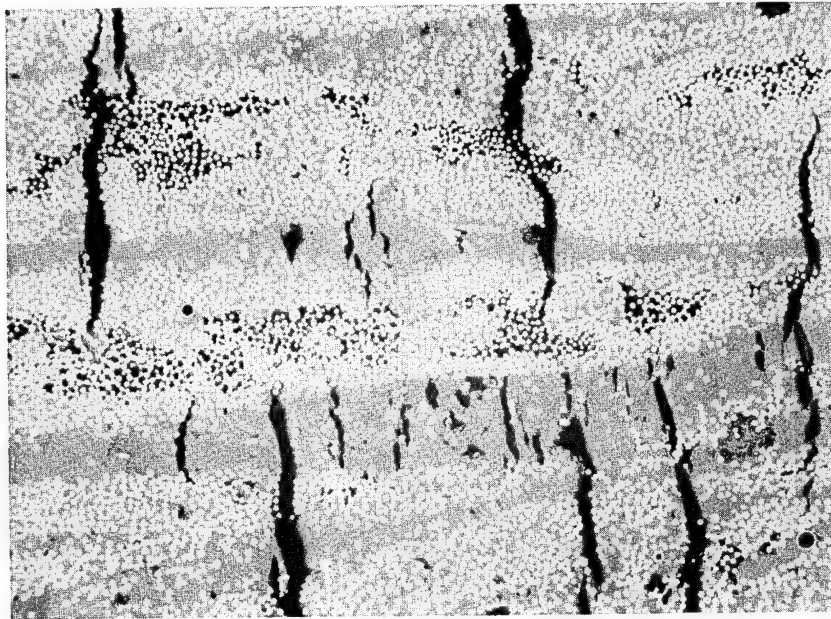
PICTURE MADE FROM AREA SHOWING POOR C-SCAN
USING 15 MHZ TRANSDUCER

PICTURE MADE FROM AREA SHOWING GOOD C-SCAN
USING 15 MHZ TRANSDUCER

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11.   BONDING HIGH QUALITY LAMINATES

In general, lap shear samples prepared using composite adherends failed by shearing within the composite. The observed strength reported, therefore, was a measure of the shear strength of the composite and not the adhesive strength. This failure within the adherend was probably partially the result of the poor quality of the composite adherends.

Although the lap shear samples prepared using composite adherends and aluminum filled adhesive solution Composition F (Table XVI) have 589 K shear strengths above the NASA goal level of 13.79 MPa (2000 psi), the R.T. lap shear strengths have been below the 20.69 MPa (3000 psi) NASA goal level with the failure in every case occurring within the composite adherend. In order to determine if this adhesive system would, in fact, give R.T. bond strengths above the NASA goal, high quality laminates 2.03 mm (80 mils) thick were prepared in-house and bonded.

Small laminates were prepared at high temperatures (673 K, 752°F) under 1.38 MPa (200 psi), cut into 25.4 mm x 101.6 mm (1" x 4") lap shear coupons and mechanical test specimens. The results of tests on the specimens are given in Table XXXI.

TABLE XXXI.

PROPERTIES OF HTS/NR-150B2 LAMINATES
PREPARED AT HIGH TEMPERATURES AND PRESSURES

Test Temp. K (°F)	Flex Strength MPa (psi)	Flex Modulus GPa (M psi)	Short Beam Shear Strength MPa (psi)
R.T.	1586.5 (230.1)	128.1 (18.58)	70.3 (10.2)
589 K (600°F)	1041.8 (151.1)	130.9 (18.97)	44.1 (6.4)

The properties of the laminates prepared in-house indicated in the table above are well above these for the composite panels indicated in Table XXX.

Lap shear samples were prepared using these laminates as adherends with the adhesive and processes indicated in Section 7.2. The lap shear strengths of these samples are indicated in Table XXXII.

TABLE XXXII.

BOND STRENGTHS OF LAP SHEAR SAMPLES
FROM HIGH QUALITY HTS/NR-150B2 LAMINATES

Test Temp.	Lap Shear Strength MP (psi)	Failure Mode
R.T.	23.42 (3397)	within composite
589 K (600°F)	15.67 (2273)	within adhesive

It can be concluded that, when high quality graphite fiber/NR-150B2 composites are bonded with the preferred NR-150 adhesive system using diglyme as the solvent, lap shear bond strengths exceeding the NASA goal levels (20.69 MPa at R.T. and 13.79 MPa at 589 K) are readily obtained.

12. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this program to develop a more easily processed aromatic polyimide resin adhesive based on NR-150 technology. Based on these conclusions, recommendations are given for further developmental work.

12.1 CONCLUSIONS

1. An NR-150 precursor adhesive solution composition was developed which gives a significant improvement in processibility over other all aromatic polyimide adhesives.

2. The new NR-150 adhesive solution composition consists of a 1:3/4:1/4 mole ratio of 2,2 bis (3',4'-dicarboxyphenyl) hexafluoropropane:paraphenylenediamine:oxydianiline; 48 wt. % cured resin solids in diglyme, containing 65% aluminum powder based on total cured solids.

3. The attainable lap shear bond strengths using the aluminum powder fiiled NR-150 adhesive solution indicated in conclusion (2) above are as follows:

Test Temp.	6/4 Titanium Substrates	Graphite Fiber/ NR-150B2 Resin Matrix Substrates	NASA Goal Levels
R.T.	24.13 MPa (3500 psi)	23.44 MPa (3400 psi)	20.69 MPa (3000 psi)
589 K (600°F)	15.13 MPa (2200 psi)	15.51 MPa (2250 psi)	13.79 MPa (2000 psi)

4. The use of diglyme as the solvent in place of the usually employed N-methylpyrrolidone results in a marked simplification of the bonding process required to produce high quality low void lap shear bonds.

5. Lap shear samples prepared using graphite fiber/ polyimide matrix adherends and aluminum filled adhesive have excellent resistance to the following environments: 1800 Ks (500 hrs.) in 589 K (600°F) air; 3024 Ks (35 days) in 322 K (120°F)

95% R.H.; 2937.6 Ks (34 days) immersed in jet fuel or methylethylketone at R.T.

6. The aluminum filled adhesive system has shown excellent resistance to crack propagation under stress at 589 K (600°F).

7. Although the new NR-150 adhesive produces wide area bonds using composite adherends having bond strengths that approach acceptable levels, under the bonding conditions used the bond lines are not void free.

8. The new adhesive system should have utility for bonding both metals and composites in applications requiring long term exposure to at least 589 K (600°F).

12.2 RECOMMENDATIONS

1. The new NR-150 adhesive solution should be optimized. The following items were not investigated in the present contract and should be evaluated:

(a) Concentration of aluminum powder filler - Although a 65 wt. % loading of aluminum was used, no effort was made to determine the optimum loading.

(b) Adhesive prepreg toughness - The adhesive prepreg used for the environmental studies was somewhat brittle. Evaluation of methods of improving its toughness should be explored.

(c) Primer coating thickness and cure - A primer coating .0254-.0508 mm (1-2 mils) thick was used for the environmental studies. The coating was "B" staged 300 secs. (5 min.) at 418 K (293°C). The use of a thinner more highly cured primer coating should be explored. Application of the primer coating by spraying should be evaluated to produce a more uniform coating.

2. The bonding and post cure procedure for preparing lap shear samples with the diglyme adhesive system is not necessarily optimized. The following process steps should be investigated:

(a) The bond time at 589 K using 1.38 MPa (200 psi).

(b) The necessity of a post cure step under full vacuum, no pressure, immediately after the bonding step.

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(c) The effect of a free standing post cure at temperatures above 589 K (600°F).

3. The dramatic improvement in processibility brought about by the replacement of NMP solvent with diglyme in the NR-150 solution suggests that there may be other solvents having greater volatility than diglyme that may result in further improvements in processibility. For example, by using a higher volatility solvent, the bonding temperature may be reduced from 589 K (600°F) to 505 K (450°F), a temperature attainable in many production autoclaves. The use of a more volatile solvent may result in an adhesive more-suitable for wide area bonding. **Solvents such as dioxane, the** monomethyl ether of ethylene glycol, dimethyl ether of ethylene glycol (glyme), and ethylene glycol are possible candidates.

4. The further investigation of the bonding of titanium as well as metals such as aluminum, stainless, and monel should be carried out. The various types of surface treatments of the metals should be scouted.

The effect of various environments on lap shear samples bonded using these adherends should be made. As the polyimides based on NR-150 solutions have excellent thermal oxidative stability at high temperatures, the exposure of bonded samples to temperatures of 589 K (600°F) to 616 K (650°F) for several thousand hours should be carried out.

5. Improved techniques for applying the diglyme based adhesive to the cell edge of a honeycomb in order to improve the flatwise tensile strength of a honeycomb sandwich panel should be sought.

6. As polyimides based on NR-150 solutions have a high degree of thermoplasticity and, therefore, toughness and resilience, adhesive bonds prepared using these new adhesive systems should be evaluated in a cyclical stress test at various temperatures, to determine their performance vs other adhesive systems and their suitability for use in applications such as jet engines.

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7. Aluminum powder was the only adhesive filler evaluated in the program. Other fillers such as glass frit, mica, alumina, and other metals and metal oxide powders should be investigated.

APPENDIX A.

PREPARATION OF SURFACE OF TITANIUM (6/4) COUPONS
FOR ADHESIVE BONDING WITH NR-150B2G SYSTEMS

(1)   "Sandblast" 6/4 titanium coupons using Norton abrasive "Dynablast" 80/100 mesh alumina in a pressure blasting apparatus to give 50-100μ inch surface roughness.

(2)   The coupons were then suspended in an ultrasonic Freon® TF bath for 10 minutes.

Using Phillips Ultrasonic Generator

Dial setting 100 switch high

(3)   Dry coupons at least 5 minutes in hood.

(4)   Dip coupons in "Pasajell" 197 with up and down strokes covering about 1" of coupon for about 1 minute.

(5)   Hang coupons in hood covered with "Pasajell" to etch for 10 minutes.

(6)   Redip coupons into "Pasajell" for 1 minute as in (4) above.

(7)   Hang coupons in hood covered with "Pasajell" to etch for another 10 minutes.

(8)   Wash coupons with hot tap water and remove "Pasajell" with acid brush then thoroughly rinse with flowing tap water.

(9)   Treat coupons suspended in an ultrasonic tap water **bath for** 5 minutes.

(10)   Allow coupons to dry in hood for 5 minutes.

(11)   Treat coupons suspended in an ultrasonic distilled water bath for 10 minutes.

(12)   Air dry coupons at R.T. for 10 minutes.

(13)   Heat coupon in oven at 70°C for 10 minutes.

(14)   Coat coupons with primer solution within 30 minutes after removal from oven.

APPENDIX B.

PRIMING OF ETCHED TITANIUM
SURFACES FOR IMPROVED ADHESION

UNFILLED ADHESIVE SOLUTIONS CONTAINING NMP

For Lap Shear Samples
Part I

(1)   Warm adhesive priming solution to ~70°C and mix thoroughly.

(2)   Using acid brush apply solution to etched titanium at or slightly above room temperature covering surface to be bonded.

(3)   Using Gardner coating knife, set at 3 1/2 mils above metal surface, remove excess solution. A uniform coating results if knife is slightly warm to touch.

(4)   "B" stage primed coupons for 5 minutes at 145°C (293°F).

For Wide Area Bonds
Part II

(1)   Warm adhesive priming solution to ~70°C and mix thoroughly.

(2)   Warm previously etched titanium surface to be bonded to 60-65°C (140-148°F).

(3)   Apply adhesive primer solution to surface with acid brush.

(4)   Before panel has cooled, remove excess coating by sliding a 1/2 inch diameter Teflon® rod across surface.

(5)   "B" stage primed panels for 10 minutes at 145°C (293°F).

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APPENDIX C.

MOLDING OF ADHESIVE PREPREG BASED ON
NMP SOLUTIONS FOR TMA ANALYSIS

(1) Stack 3 to 6 plys of 25.4 mm x 25.4 mm squares of adhesive prepreg in press, preheated to 700 K (800°F).

(2) Preheat at 700 K, touch pressure for 120 s (2 minutes).

(3) Consolidate at 13.79 MPa (2000 psi) for 60 s (1 minute) at 700 K.

(4) Devolatilize for 600 s (10 minutes) touch pressure at 700 K.

(5) Mold for 300 s (5 minutes) at 13.79 MPa (2000 psi) at 700 K.

(6) Vent for 300 s (5 minutes) at touch pressure and 700 K.

(7) Cool rapidly under 1.38 MPa (200 psi).

APPENDIX D.

PREPARATION OF ADHESIVE PREPREG
USING NR-150 ADHESIVE SOLUTIONS
BASED ON NMP
CONTAINING ALUMINUM POWDERS

Glass Cloth Scrim Coated Two Successive Times

First Coating

(1) Warm adhesive solution to 353 K (176°F) to reduce viscosity
of aluminum filled solution.

(2) Soak glass scrim cloth (112 Style E glass ~3.5 mils thick) in
adhesive solution at temperature, turning cloth over to ensure
complete wetting of cloth.

(3) While solution on cloth is still warm, pass coated cloth
between opposed Gardner coating knives set at an air gap of 15 mils.

(4) Clamp prepreg edges in frame to prevent wrinkles in cloth and
place in preheated air oven. Heat 12 Ks (20 mins.) at 418 K (293°F)
then 0.6 Ks (10 mins.) at 433 K (320°F).

(5) A 6-7 mil thick prepreg results having a volatiles content of
6.3-6.5%.

Second Coating

(6) Soak prepreg from first coating in adhesive solution at 353 K
(176°F) for 1.8 Ks (30 mins.) after 0.9 Ks (15 mins.).

(7) While solution on prepreg is still warm, pass prepreg between
opposed Gardner coating knives set at an air gap of 35 mils.

(8) Place prepreg in frame and place in preheated oven at 418 K
(293°F) for 1.8 Ks (30 mins.).

(9) The resulting prepreg is 12-16 mils thick and has a volatiles
content of 7.5 to 9.0% measured by the weight loss after 1.8 Ks (30
mins.) at 644 K (700°F).

APPENDIX E.

PROCEDURE FOR PRIMING COMPOSITE ADHERENDS
USING NR-150 ADHESIVE SOLUTIONS
BASED ON DIGLYME

(1) The faying surfaces of the composite lap shear coupons are lightly sanded, first in the long (fiber) direction and then in the cross direction using 80D grade sandpaper.

(2) 65 wt. % aluminum powder (Reynolds Grade 1-131 atomized) is added to the experimental NR-150 adhesive solution then warmed to 343-353 K (158-176°F) and stirred well to ensure complete mixing of the ingredients. (To each 100 grams of solution, add 89.14 grams of aluminum powder.)

(3) Using an acid brush (or equivalent), apply the warmed solution to the previously sanded surfaces using a minimum amount of solution.

(4) "B" stage the coated lap shear samples in an air circulated oven first for 5 minutes at 358 K (185°F), then 5 minutes at 373 K (212°F), then 5 minutes at 393 K (248°F), and finally for 5 minutes at 418 K (293°F).

(5) A primer coating thickness of .025-.051 mm (1-2 mils) is obtained from the above procedure.

PROCEDURE FOR PRIMING TITANIUM
ADHERENDS PREVIOUSLY ETCHED

Follow Items 2-5 above.

APPENDIX F.

PREPARATION OF ADHESIVE PREPREG
USING NR-150 ADHESIVE SOLUTIONS
BASED ON DIGLYME

(1) To the experimental NR-150 adhesive solution add 65 wt. % (based on total cured solids) aluminum powder, Reynolds Grade 1-131 atomized or equivalent. (To each 100 grams of solution add 89.14 grams of powder.) Warm solution to 343-353 K (158-176°F) for ease of mixing.

(2) Soak a piece of 112-38 Style E glass with a I-621 finish (or equivalent) in the warm solution, then pass the impregnated cloth between opposed Gardner coating knives (or equivalent) having a .330 mms (13 mil) air gap.

(3) Heat the impregnated cloth in a forced air circulated oven for 40 minutes at 358 K (185°F), then 20 minutes at 373 K (212°F), and then 20 minutes at 393 K (248°F). Prepreg .152-.178 mms (6-7 mils) thick containing about 10% volatiles is produced.

(4) Resoak the "B" staged prepreg in the warm adhesive solution, then pass the reimpregnated cloth between opposed coating knives having a .686 mm (27 mil) air gap.

(5) Heat the reimpregnated cloth in a forced air circulated oven for 40 minutes at 358 K (185°F), and then 20 minutes at 373 K (212°F).

The resulting prepreg is .279-.292 mm (15.0-15 1/2 mils) thick and contains 11-11 1/2% volatiles. The volatiles content is obtained by measuring the weight loss after exposing a sample of the prepreg to 644 K (700°F) for 900 seconds (30 mins.).

APPENDIX G.

PROCEDURE FOR
BONDING COMPOSITE LAP SHEAR SAMPLES
USING AN EXPERIMENTAL NR-150 ADHESIVE
BASED ON DIGLYME

(Simulated Autoclave Using a Press)

(1) Assemble the primed lap shear coupons and adhesive prepreg in a suitable holder for producing a .127 mm (1/2 inch) overlap.

(2) Place in vacuum bag in press at room temperature and use the following bonding cycle:

(a) Heat at .033 K/sec. (5°F/min.) under full vacuum and 1.38 MPa (200 psi).

(b) Hold for 3.6 Ks (1 hour) at 589 K (600°F) under full vacuum and 1.38 MPa (200 psi).

(c) Hold for a second 3.6 Ks (hour) at 589 (600°F) under full vacuum only.

(d) Cool press rapidly using water through platens using full vacuum only.

(3) Post cure bonded samples 15.6 Ks (16 hours) (overnight) free standing in air at 589 K (600°F).

APPENDIX H.

PREPARATION OF ADHESIVE PREPREG
BASED ON DIGLYME SOLUTIONS
FOR WIDE AREA BONDING

(1) To the experimental adhesive solution add 65 wt. % (based on total cured solids) aluminum powder, Reynolds Grade 1-131 atomized or equivalent. (To each 100 grams of solution, add 89.14 grams of powder.) Warm solution to 343-353 K (158-176°F) for ease of mixing.

(2) Soak the glass scrim carrier cloth (112 Style E glass, I-621 finish, or equivalent) in the warm (322-333 K, 130-150°F) solution.

(3) Pass the impregnated cloth between opposed Gardner coating knives (or equivalent) having a .457 mm (18 mil) air gap.

(4) Heat impregnated cloth in air circulated oven for 40 minutes at 85°C and then 15 minutes at 100°C.

The above procedure produces adhesive prepreg about .229-.241 mms (9-9 1/2 mils) thick having a 10.3-10.5% volatiles content. The volatiles content is obtained by measuring the weight loss on exposing a sample of the prepreg to 644 K (700°F, 371°C) for 30 minutes.

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15. Supplementary Notes

Langley Technical Monitor: Terry L. St. Clair
Final Report

16. Abstract   This final report describes the work performed to develop an adhesive based on DuPont's NR-150 polyimide precursor solutions which is more easily processed than conventional aromatic polyimide systems and shows potential for use for extended times at 589K (600°F). The newly developed adhesive system is based on a solution containing diglyme as the solvent and 2,2 bis(3',4'-dicarboxyphenyl)hexafluoropropane, paraphenylenediamine, and oxydianiline. The replacement of N-methylpyrrolidone with diglyme as the solvent was found to improve the adhesive strengths of lap shear samples and simplify the processing conditions for bonding both titanium and graphite fiber/polyimide matrix resin composites. Information was obtained on the effects of various environments including high humidity, immersion in jet fuel and methylethylketone on aluminum-filled adhesive bonds. The adhesive was also evaluated in wide area bonds and flatwise tensile specimens using titanium honeycomb and composite face sheets. This study indicates that this newly developed adhesive system has the potential for use in applications requiring long term exposure to at least 589K (600°F).

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